

# Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 27, SEC. F.

NOVEMBER, 1949

NUMBER 11

## MILD OXIDATION OF ALKALI LIGNINS<sup>1</sup>

By R. A. V. RAFF<sup>2</sup> AND G. H. TOMLINSON II<sup>3</sup>

### Abstract

Following the discovery that the reinforcement of GR-S rubber by alkali lignins is greatly enhanced if the lignins, prior to their coprecipitation with the latex, are subjected to oxidation, the reaction of alkali lignins with oxygen and the properties of oxidized lignins were studied. It was found that particularly the melting points of the lignins and their lyophilic properties are increased by continued oxidation. This suggested that these two properties are mainly connected with, and possibly responsible for, the reinforcing capacity of the oxidized lignins in the rubber, which in turn is correlated with particle size, surface area, and adsorptive power. It could also be established that, providing definite coprecipitation conditions are maintained, a well defined oxidation range exists, over which lignins display optimal reinforcing properties.

### Introductory Remarks on the Importance of Oxidation Studies on Alkali Lignins

The early stages of development work at Howard Smith Paper Mills Limited on the use of alkali lignin in plastics have shown that the recovery and separation of the lignin from black liquor should be carried out under conditions such as to minimize reaction of the lignin with oxygen from the air. Progressive oxidation was found to increase the lyophilic properties of the wet lignin. This was undesirable from the standpoint of filtering and drying. It also increased the melting point and reduced the flow properties of the dry lignin. This made the latter less suited for molding purposes.

On the other hand, in joint work with Polymer Corporation, Sarnia, Ontario, on the use of alkali lignin as a reinforcing agent for GR-S rubber, it was discovered that reinforcement was greatly enhanced with increasing oxidation (4, 5).

It was thus realized that the reaction of alkali lignins with oxygen would have to be investigated and the properties of oxidized lignins studied. It should be pointed out that the investigation reported here does not include the oxidation of lignosulphonic acids, i.e., of waste sulphite liquor, nor the formation of vanillin.

<sup>1</sup> Manuscript received June 8, 1949.

Contribution from the Research Department of Howard Smith Paper Mills Ltd., Cornwall, Ontario.

Paper presented before the Wood Chemistry Section of the Canadian Pulp and Paper Association, in Niagara Falls, on June 3, 1949.

<sup>2</sup> Research Chemist, now Senior Fellow at Mellon Institute, Pittsburgh, Pa.

<sup>3</sup> Research Director.

### Reference to Previous Publications in Relation to the Present Problems

As far as the earlier literature on the oxidation of alkali lignin is concerned, the well known books of Fuchs, and Freudenberg, and the article of Max Phillips in "Chemical Reviews", 1934, adequately cover such work up to about 1934. Phillips, in his monograph, points out that the published results on the oxidation of lignin throw little light on the structure of lignin since, even by "mild" oxidation, complete disruption of the molecule is said to take place, resulting in simple degradation products only. This indeed, also applies to most of the more recent publications. Even in the few cases where milder and more controlled oxidation conditions were applied, the main interest of the investigators was in the low molecular degradation products rather than in the remaining lignin skeleton.

Franz Fischer and coworkers (2) reported as early as 1922 that lignin in the presence of alkali is capable of taking up oxygen, particularly at increased pressures and temperatures, whereby he distinguishes between mild and strong oxidations.

Freudenberg, in his book, expresses the belief that mild oxidation of lignin causes the formation of carboxyl groupings, which render the molecule soluble in alkali, without considerably changing its internal structure. Stronger oxidation, however, is said to always lead to simple degradation products, without the possibility of isolating intermediates.

A few of the more recent papers deal also with the changes in the lignin molecule caused by mild oxidation.

Walde and Hixon (7) found that the reaction of ammonia lignin from oat hulls with alkaline iodine solution could be made quantitative. Iodoform was found among the degradation products, the oxidized lignin itself containing iodine and carboxyl groups. Different preparations of lignins gave different titration values, ranging from 68 cc. of *N*/10 iodine solution per gm. sample for sulphuric acid lignin from aspen to 190 cc. for ammonia lignins from oat hulls. When the latter lignin had been pretreated with Fehling's solution, the titration value decreased to 154.

This indicates that the oxidation values for lignin vary considerably, the actual values depending on the method of preparation and pretreatment of the lignin sample. The amount of copper reduced (3) was not found to parallel the loss in iodine oxidation value. The oxidation of lignin with alkaline solutions was further found by Walde and Hixon to be peculiar in that the methoxyl content decreases from 12.5 to approximately 7.4%, while the iodine entering the molecule accounts for only 1.1% of the decrease.

A valuable contribution to the problem of lignin oxidation was made by Bennett of the Massachusetts Agricultural Experimental Station, in a paper entitled "Some Acidic Properties of Alkali Lignin" (1). The article deals

primarily with the possible role of lignin in the absorption of minerals by plants.

Since Bennett felt that increases in base exchange values of soil organic matter may be caused partly by progressive oxidation, samples of corncob lignin were subjected to oxidation with alkaline iodine solutions. Oxidation values of 172 cc. of *N*/10 iodine per gm. of lignin were obtained, and among the degradation products, iodoform was detected, a finding similar to that of Walde and Hixon. The oxidized lignin appeared to be considerably more highly peptized, and base exchange determinations on the electrolyzed product indicated an increase of about 35%, probably due to the presence of carboxyl groups.

A method that could possibly be developed into a procedure for determining the reducing capacity of lignins has been reported recently by Schuerch (6, p. 19). In an attempt to find a method for modifying periodate lignin to render it soluble, oxidations at 20° C. with aqueous chromium trioxide buffered to pH 0.5 seemed to show some promise. After about 17 atoms of oxygen had been taken up per 1000 gm. of lignin, the reaction slowed down and the lignin became soluble in alkali. The precipitated, washed, and dried product consumed only eight atoms of oxygen when subjected once more to the same treatment.

### Preparation of Lignins of Varying Degrees of Oxidation

In our own work, the oxidized alkali lignin for use in reinforcing rubbers was generally prepared by heating a solution of the sodium lignin salt in water, or a solution of the acid precipitated lignin in caustic, and bubbling oxygen or air through these solutions. The tendency of these solutions to turn acid was counteracted by the addition of sodium hydroxide during the oxidation.

In the course of this work it was necessary to prepare considerable quantities of oxidized lignin for laboratory and pilot plant coprecipitations with the rubber latex. At various stages in this development the oxidation was carried out in a 40 gal. drum, in a type N Roto-Clone, and in a small tower (40 in. diam., 7 ft. high). Because of the somewhat different methods of air-liquid contact employed, the time required to obtain a lignin of suitable reinforcing properties was found to vary over a considerable range.

### Changes in Lignin Characteristics Depending on the Degree of Oxidation

It was considered to be highly desirable to establish physical and/or chemical characteristics of the lignin at various stages in the oxidation that could then be related to the reinforcing properties when the lignin was coprecipitated with rubber. A knowledge of the change of the amount of oxygen consumed, corresponding to any given change in these characteristics, was also considered desirable.

### (a) *Melting Points*

One of the most characteristic changes in property is the increasing melting point that is obtained with isolated lignins that have been subjected to progressive oxidation. This increase in melting point is a fairly satisfactory criterion of the degree of oxidation of a lignin sample, so long as it is kept in mind that other reactions, like chlorination, also raise the melting point of lignin, but do not increase its reinforcing properties.

Some points should be noted regarding the determination of the melting point of lignins, which is somewhat less definite than in the case of most low-molecular, crystalline compounds.

One method of determining the melting point of lignins is carried out in the usual Thiele melting point apparatus, using open capillaries, and cottonseed oil as a heating fluid. The lignin sample is finely ground and predried for about 30 min. in an air oven at 105° C., under which conditions no noticeable oxidation takes place. A small quantity of this lignin is then filled into the capillary, without removal of the sample from the oven. The filled capillary is then attached to a thermometer and inserted in the melting point apparatus, which has been heated previously to around 90° C. From then on, the temperature of the bath is slowly and evenly raised, and the sample observed under strong illumination. Generally, lignin samples show a definite shrinkage at a certain temperature, which is noted. Heating beyond this point causes the lignin in most cases either to show definite melting at a definite temperature, or at least to flow together and to wet the walls of the capillary. The temperature at which either or all of these changes occur is taken as the melting point of the sample, although very often no real melting can be observed. Detailed data of the relation between oxidation and the results obtained by this "open tube method" will be presented later in Table V. It is sufficient to mention now that, for example, for a medium-oxidized lignin (i.e., medium, from the viewpoint of rubber reinforcement) the data observed for shrinkage and melting point, respectively were: 214° C. and 228° C.

In search for a more accurate method of determining melting points of lignins, it was thought that volume changes occurring while the sample is being heated could be more easily followed by covering the sample in the capillary with a small amount of mercury and observing the meniscus of the latter. Somewhat larger tubes were found to be more suitable, in which the dried and finely ground lignin was packed tight to a height of 25 mm. and covered with a column of mercury 10 mm. high.

Attaching this tube to the thermometer, inserting it in the preheated melting point apparatus, and gradually increasing the temperature, reveals in most cases three clearly observable points at which changes occur. The above mentioned, moderately oxidized lignin showed, for example, that the mercury level was first raised by increasing the temperature, but then, at 177° C., it suddenly dropped. This point was marked as "shrinkage". Continued



heating caused the mercury level to eventually rise again, until a point was reached at which the lignin sample in the tube turned jet black and glossy, with signs of wetting the wall of the tube. This point (210° C. in the case noted) was called the melting point by this method. Further heating of the sample led to a slight additional rise in level of the mercury. Then, fairly suddenly, gas developed from the lignin sample, forcing its way as bubbles through the mercury. This, in the present case, took place at 224° C., and seemed to be a sign of decomposition or at least of structural changes in the lignin molecule. Thus, the lignin sample by this method gave three characteristic points.

Experiments with the electrically heated melting point apparatus of the Fisher-Johns type gave only one point, at which signs of melting or fusing of the lignin sample were noted. A slight pressure with a needle on the cover glass made it fairly easy to observe that the sample turned, at 213° C., to a jet-black sticky tar.

A comparison of these results, as obtained on the same lignin by the three methods, is shown in Table I.

TABLE I  
COMPARISON OF RESULTS OBTAINED BY VARIOUS MELTING POINT METHODS

Method	Characteristic changes		
Open-tube method		Shrinkage 214° C.	Melting 228° C.
Mercury-covered tube method	Shrinkage 177° C.	Turns black 210° C.	Gas developed 224° C.
Electric stage method		Melting 213° C.	

It would appear from this table that the point of shrinkage observed by the "open-tube method", the point at which the sample turns black in the "mercury-covered tube method", and the melting point observed by the "electric stage method", take place at approximately the same temperature, whereas the melting point by the open-tube method seems to correspond to the point at which gas development is observed in the "mercury-covered tube method".

This agreement is not always as good as in the example shown. More of these figures will be given in Table V. Particularly in the range of "over-oxidized" lignin (that is, from the viewpoint of rubber reinforcement) the agreement is often very poor, even for results obtained on the same sample by the same observer and the same method, regardless of the method used.

As a routine test it was found best to carry out melting point determinations on the same sample by all three methods and to attempt to obtain the above correlation between them.

One interesting fact has been discovered in the course of these investigations, namely, that lignin gives off gases at its melting point. This has been previously overlooked, since melted lignin samples, on remelting, showed essentially the same melting point, and lignin was thus considered to be a true thermoplastic material. Such conclusions should be reconsidered in the light of these recent findings. This thermodecomposition of lignin, which may play an important role during molding when lignin is used in plastics and laminates, has been made the subject of a separate study, results of which will be reported at a later date.

*(b) Filter Time and Water Retention*

Any increase in melting point of lignin that is due to oxidation is normally accompanied by an increase in the lyophilic properties of the lignin. This change in properties can be observed in several ways. For example, if solutions of lignins of increasing degree of oxidation, but of the same lignin content, are precipitated with acid at 90° to 95° C., the slurries will filter more slowly the higher the degree of oxidation of the lignin. Further, the lignin cake containing the more highly oxidized lignin will also hold more water. Corresponding results are obtained when coprecipitates with GR-S latices are involved.

Unoxidized lignin can be precipitated in such a way that a fast filtering precipitate is obtained, at a temperature as low as 70° C. However, oxidized lignin, when precipitated at such a low temperature, is hardly filterable. With such lignins, higher precipitation temperatures should be used in order to obtain a product filterable at a reasonable speed, although even under optimal conditions filtering is always slower than with the less oxidized or the unoxidized lignin sample.

Filter times of samples containing standard amounts of lignins, and precipitated under standard conditions, as well as the water contents of the filter cakes, with or without latex, have been used successfully to characterize lignin samples and to check on the progress of lignin oxidations.

*(c) Changes of Viscosity in Solution*

The increase in viscosity due to oxidation of solutions of lignin in cellosolve has already been reported (4, 5). However, the changes observed are too small to form the basis of a routine test.

*(d) Changes in Methoxyl Content*

The same applies to the change in methoxyl content, which shows a definite, but small decrease with progressing oxidation, at least in the investigated range.

*(e) Reduction of Fehling's Solution*

The fact that lignin preparations reduce Fehling's solution has been observed by Powell and Whittaker (3). There is definite indication that the ability of a lignin to reduce Fehling's solution, as measured by the amount of cuprous

oxide deposited under standard conditions, decreases with increasing degree of oxidation. But again, the differences are none too great, and the individual and experimental variations are considerable.

(f) *Titration Values with Iodine Solutions*

The titration values of lignins with iodine solution when carried out according to the method of Walde and Hixon (7), also show a definite, but none too great, decrease with increasing degree of oxidation.

(g) *Acidmetric Titration Curves*

A comparison of the titration curves for unoxidized and moderately oxidized deciduous alkali lignins is shown in Fig. 1. In each case, 1 gm. of the moisture-

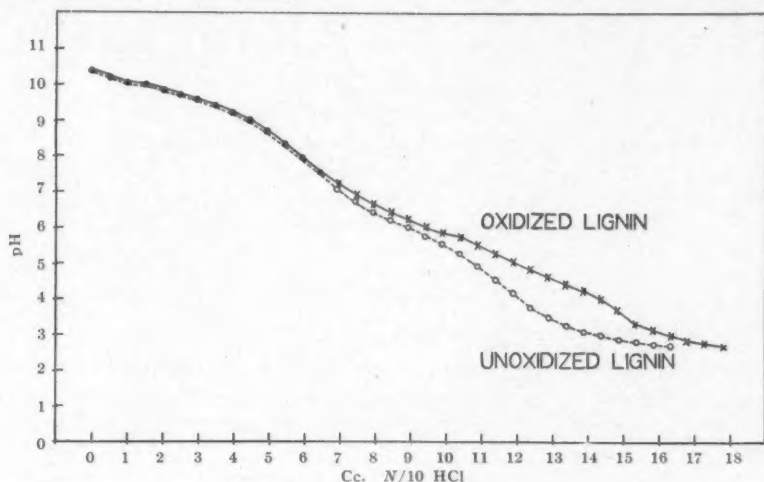


FIG. 1. Titration curves.

free lignin was dissolved in 1.34 cc. of  $N/1$  sodium hydroxide, and the solution was diluted to 100 cc., and titrated with  $N/10$  hydrochloric acid. The comparison of both curves shows the increased acidic nature of the oxidized lignin.

Unfortunately the inflection points are difficult to locate accurately. However, an approximation of the equivalent weight as based on the carboxyl group can be calculated and the following results are obtained:

	Unoxidized	Oxidized
Approx. pH 1st inflection point	8.0	8.0
" " 2nd "	4.0	3.75
cc. $N/10$ HCl/gm. lignin	6.4	8.8
Approx. milliequivalent/100 gm.	64	88
Approx. equivalent weight, based on carboxyl group	1560	1135

(h) *Bicarbonate-neutralization Capacity of Lignins*

Another method of determining carboxyl groups is based upon base exchange, as worked out for cellulose by Wilson (8). This method was adapted for use in the analysis of lignin. The dried and finely ground weighed sample is suspended for two hours in dilute hydrochloric acid, filtered, washed until neutral, resuspended in 100 cc. of a solution containing  $N/100$  sodium bicarbonate and  $N/10$  sodium chloride, left in contact for one hour, then the lignin filtered off, and the solution back-titrated with dilute hydrochloric acid. From this, the "base-binding" ability of the lignin is calculated in milliequivalents per 100 gm. moisture-free lignin, as follows:

Carboxyl (as milliequivalents per 100 gm. lignin)

$$= \frac{100}{25G} \times \left( b - a - \frac{v.a}{100} \right),$$

where  $G$  = weight of m.f. lignin, in grams;

$v$  = amount of moisture in lignin, in grams;

$a$  = number of ml. of  $N/100$  hydrochloric acid consumed by 25 ml. test solution at end of experiment;

$b$  = number of ml. of  $N/100$  hydrochloric acid consumed by 25 ml. sodium bicarbonate solution before start of experiment.

The above formula is calculated for the case where the lignin sample is suspended in 100 cc. of the sodium bicarbonate-sodium chloride solution, but where only 25 cc. of it is used in the back-titration.

An investigation of this method as applied to lignin indicated that equilibrium was approached at a very slow rate, so that the one hour test, as used by Wilson for cellulose, could not be used as an index of the actual carboxyl content.

In Table II are given data showing the effect of time and quantity of bicarbonate on the values obtained. Both dried and freshly precipitated samples of unoxidized and oxidized deciduous alkali lignins were used. It was observed that the immediate bicarbonate neutralizing capacity was considerably greater with the oxidized samples but that this differential was partially reduced after several days.

It should be borne in mind that neutralization values of 64 and 88 milliequivalents per 100 gm. for the oxidized and unoxidized lignins respectively were obtained by titration of aqueous solutions of the sodium salts. It is thus apparent that the bicarbonate neutralization test is influenced by not only the true carboxyl content but its accessibility in the solid phase, the rate of which is determined by the slow diffusion process.

It was noted that with the one hour test, values of the order of 4.0 milliequivalents per 100 gm. were obtained with unoxidized samples, as compared to values of around 20 to 22 for even mildly oxidized samples. The latter value

TABLE II  
 CARBOXYL DETERMINATIONS ON LIGNINS UNDER VARYING CONDITIONS

Type of lignin	Unoxidized			Oxidized		
	2.5 gm. of lignin susp. in $\text{NaHCO}_3$ . NaCl		Carboxyl, milliequiv. /100* gm.	2.5 gm. of lignin susp. in $\text{NaHCO}_3$ . NaCl		Carboxyl, milliequiv. /100* gm.
	Quantity, cc.	Time, hr.		Quantity, cc.	Time, hr.	
Dry	100	1	4.05	100	1	22.57
	"	4	9.00	"	4	24.92
	"	16	14.22	"	16	28.68
	"	22	14.62	"	22	30.17
	"	46	20.82	"	46	31.30
	500	1	4.00	500	1	28.15
	"	4	9.29	"	4	29.88
	"	16	18.07	"	16	33.70
	"	22	20.34	"	22	36.30
	"	46	25.07	"	46	41.79
Wet (freshly precipitated)	100	1	8.86	100	1	18.93**
	"	16	17.59	"	22	21.46**
	500	1	7.27	500	1	31.70**
	"	22	19.91	"	22	20.96**

\*See also Table V.

\*\*Samples difficult to filter, thus impairing reproducibility of results.

did not increase with increasing oxidation, as did the lyophilic properties, as will be later shown in Table V. Such a test may prove useful for distinguishing between so-called unoxidized lignins for use in plastics, and other lignins that have received more or less oxidation treatment.

#### (i) Ion Exchange Experiments

Similar conclusions with regard to the accessibility and increased acidity of the oxidized lignin can be drawn from ion exchange experiments. Weighed crystals of calcite were added to aqueous 10% suspensions of unoxidized and moderately oxidized deciduous alkali lignins, which were kept in a constant temperature bath at 25°C. At intervals these crystals were taken out, washed, dried, weighed, and returned to the lignin suspensions.

As seen in Fig. 2, the calcite crystals in contact with the suspension of the oxidized lignin lost weight much faster than the ones left with the unoxidized lignin, or, in other words, oxidized lignin is a better ion exchanger than unoxidized lignin. This observation has already been made by Bennett (1), who drew from it his conclusions as to the mechanism of humus formation in the soil.

The above reported ion exchange experiment was interrupted after 199 days and the lignins were filtered off and analyzed. A comparison of the lignin characteristics at the start of the experiment and after 199 days is given in Table III.



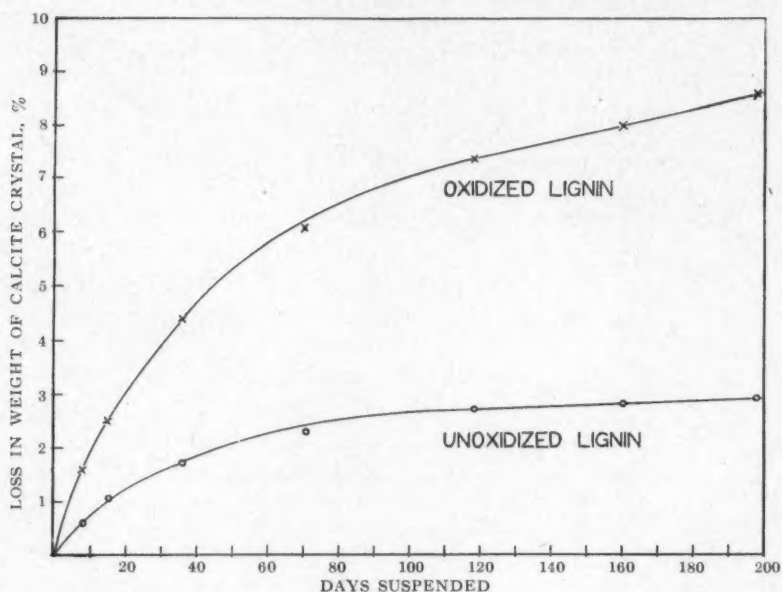


FIG. 2. Ion exchange tests.

TABLE III  
ION EXCHANGE TESTS  
(Averages from triplicates)

Type of lignin used	At start of experiment							
	% ash anal.	Melting points, ° C.						pH of susp.
		Open tube method		Mercury-covered tube method			Electric stage	
		Shrink	Melt.	Shrink	Black	Gas		
Unoxidized	0.33	160	170	157	161	168	157	6.28
Oxidized	0.53	215	228	186	216	223	213	5.94

Type of lignin used	After contact with calcite crystals for 199 days at 25° C.								
	% Ash		Melting points, ° C.					pH of susp.	
	Anal.	Calcd. from loss in wt. of crystals*	Open tube method		Mercury-covered tube method				Electric stage
			Shrink	Melt.	Shrink	Black	Gas		
Unoxidized	1.01	1.20	175	183 Above 250	168	172	175	171 Above 300	6.70
Oxidized	2.21	2.48	None	250	265	295	304	300	6.31

\*The amounts of ash found in the samples at the start of the experiment were added to the amounts of ash to be expected from the loss in weight of the suspended calcite crystals.

Both the melting point and the ash content of the lignins showed increased values after treatment with the calcite crystals, the oxidized lignin showing the greatest changes. The increases in ash content are proportional to the losses in weight of the suspended calcite crystals. The suspensions of the oxidized samples at the start as well as at the end of the experiment show a lower pH than do those of the unoxidized samples.

### Volumetric Measurements of the Lignin-Oxidation Reaction

#### (a) Equipment and Procedure

A closer study of the oxidation reaction of lignin necessitated a more exact technique than that used when lignin batches are oxidized in the preparation of lignin-rubber coprecipitates for compounding, curing, and testing.

The equipment in which these experiments were carried out is shown in Fig. 3. An amount of air-dry lignin, corresponding to 2.63 gm. moisture-free

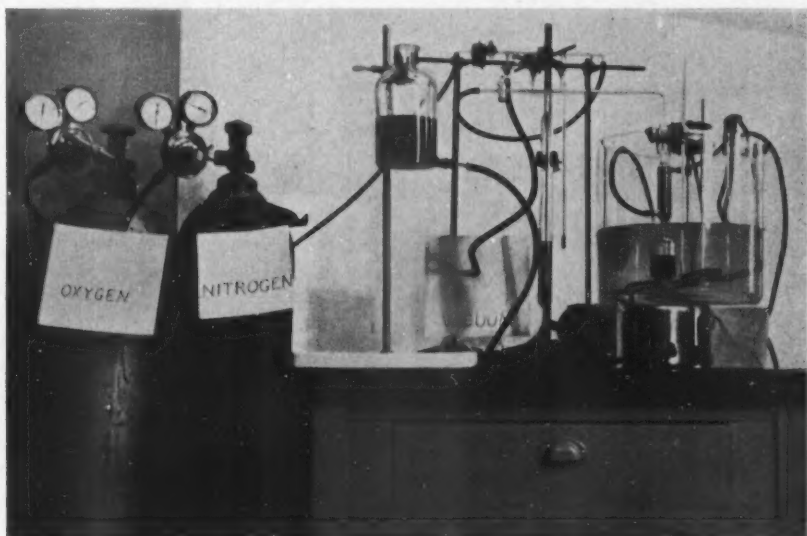


FIG. 3. Apparatus used for volumetric determination of oxygen absorption.

weight, was placed in a glass bulb, 3 in. high and  $1\frac{1}{2}$  in. wide. To this was added 13.15 gm. of a solution of sodium hydroxide, containing 20 gm. sodium hydroxide in 1000 cc. This yielded a solution containing 10% lignin and 1% sodium hydroxide, with an initial pH of approximately 11. A small magnetized stirring bar was introduced, which allowed the solution to be stirred magnetically from outside. The bulb was inserted in a constant temperature bath and connected with one arm of a gas burette. The other arm of the gas burette led to a mercury gauge and from there to a manifold, the four

outlets of which were connected with the open air, the vacuum pump, a nitrogen cylinder, and an oxygen cylinder, respectively. The liquid used as a seal was a concentrated solution of sodium chloride.

The experiment was started by repeatedly evacuating the whole apparatus and refilling it with nitrogen. Then the bath was brought up to the reaction temperature, in most cases 70° C., and the lignin sample kept under nitrogen until constancy of the volume, as read on the gas burette, indicated that constant temperature conditions had been established and that no leakage occurred. The apparatus was then repeatedly evacuated and refilled with oxygen. The vessel containing the sealing liquid was then adjusted to such a height that the distance between the surface of the liquid and the meniscus in the gas burette was 8 in., this distance being kept constant during the run. The surface of the sealing liquid and the meniscus in the gas burette were then brought to equal level, the first reading on the gas burette was taken, and the time counted from there on. This and later volume readings were converted to 0° C., and 76 cm. pressure, and the volume changes converted into grams of oxygen. The results were evaluated by relating the number of grams of consumed oxygen to the weight of the lignin sample, and reported in grams of oxygen absorbed by 100 gm. of lignin, i.e., as % oxygen absorbed.

It has already been mentioned that lignin solutions, while being oxidized, undergo a drop in pH. Basically, two ways of oxidizing lignin solutions can be visualized. Either the pH of the lignin solution is allowed to drop during oxidation, or such a drop is prevented by continually adding caustic while oxidizing. The latter method was used when preparing the oxidized lignins described in Table V, since it was found that a drop in pH causes the oxidation to gradually slow up to an extent that was found to be impractical.

However, in some of the volumetric oxidations discussed here, the pH was allowed to drop. Volume readings were taken at various intervals and converted as previously described.

In other of the volumetric experiments, where the pH was kept at its original value of about 11 during the whole experiment, the apparatus was repeatedly evacuated and refilled with nitrogen after each two hours of running with oxygen. After the oxygen had been replaced by nitrogen, the reaction vessel was opened, a predetermined amount of sodium hydroxide solution was added, and the reaction vessel again connected with the gas burette, repeatedly evacuated, and refilled with oxygen. A new volume reading was taken and the reaction allowed to proceed undisturbed for another two hours, after which time the procedure was repeated. The amount of sodium hydroxide to be added each time had to be determined in separate experiments, since the described setup did not allow a direct pH observation.

Each of these oxidations was carried on for a certain number of hours. The oxidation was then stopped by replacing the oxygen by nitrogen, and again making certain of absence of any leakage by observing the stability of the meniscus of the gas burette over a period of one to two hours.

The contents of the reaction bulb was then diluted and the pH measured. In those series in which the pH had been maintained during the run by continuous addition of sodium hydroxide, the pH at the end of each fairly long run was found to be close to the original value of 11. The lignin solution was then acidified to a pH of approximately 2.5, heated to 90° C., filtered, and the washed lignin dried in the open air and then for 30 min. at 105° C. With these samples, melting point determinations were carried out, and after redissolving in sodium hydroxide and mixing with rubber latex, lignin-containing rubber crumbs were coprecipitated.

(b) *Oxidation Rates at 70° C.*

In experiments with deciduous alkali lignin, in which the pH was allowed to drift during oxidation, results as shown in Fig. 4 were obtained. Oxygen

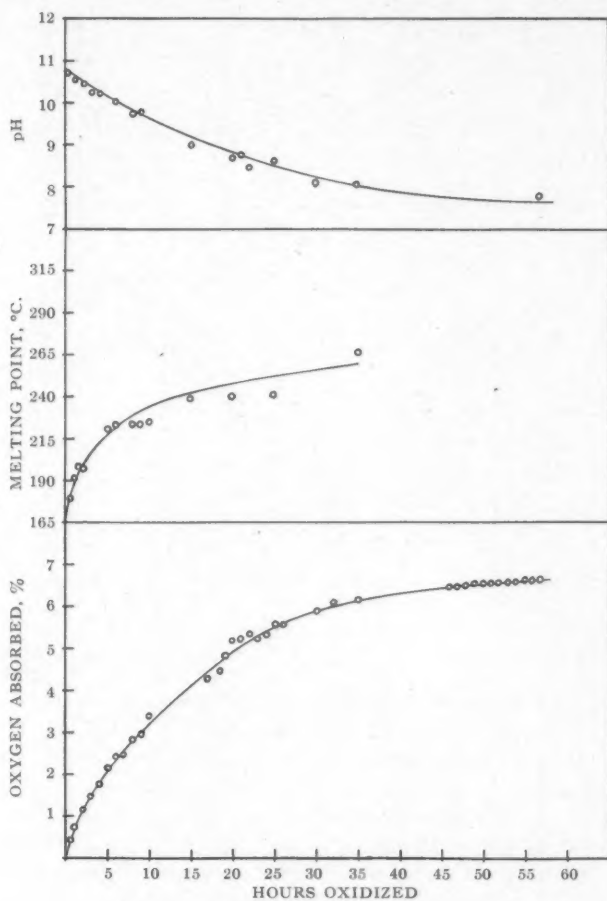


FIG. 4. Oxidation at 70° C.—pH drift.

is absorbed at a fairly constant rate for the first 20 hr. This absorption is accompanied by a drop of pH from its initial value of 10.8 to approximately 9, and an increase occurs in the melting point of the lignin to approximately  $245^{\circ}\text{C}$ ., as determined by the open-tube method. Owing to the lower pH, the oxidation then slows up considerably, and so does the rate of decrease in pH.

The progress of the reaction is quite different if the pH of the lignin solution is kept at its original value of around 11 during the whole oxidation by regular additions of small amounts of sodium hydroxide. As Fig. 5 shows, the rate

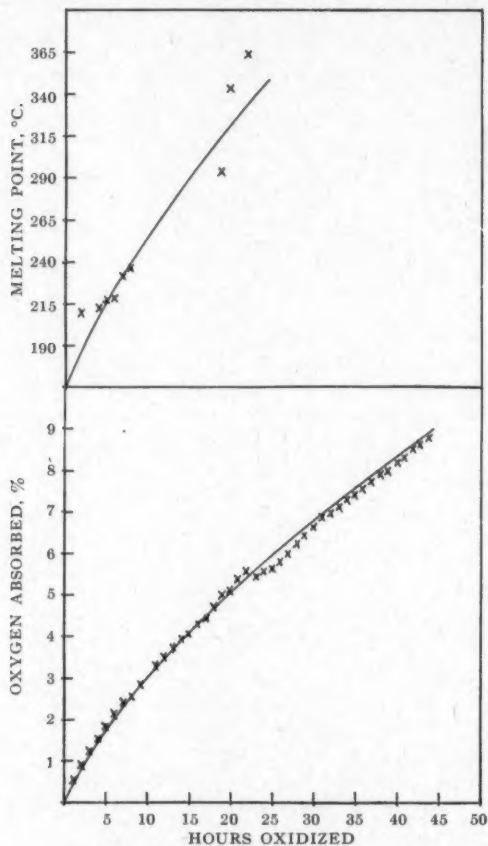


FIG. 5. Oxidation at  $70^{\circ}\text{C}$ .—pH constant.

of oxygen absorption is fairly constant over the investigated range, with only slight signs of slowing up as the absorption progresses. The melting point curve follows the same pattern, and lignins with high melting points are obtained at a fairly early stage of the oxidation.



By plotting the melting points and the pH values against the percentage of absorbed oxygen for both series together in one graph, Fig. 6 is obtained. This figure reveals the rather surprising effect that the same percentage of absorbed oxygen raises the melting point of the oxidized lignin considerably higher when the pH was kept constant during the oxidation than when it was allowed to drop.

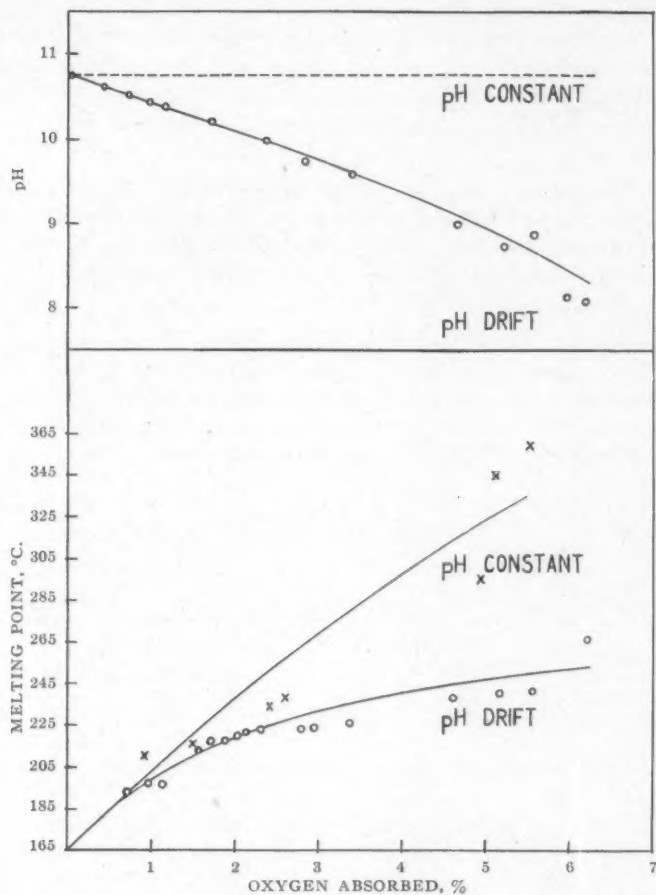


FIG. 6. Oxidation rate vs. pH.

In other words, higher pH in the lignin solution not only increases the speed of the oxidation, which results in a higher absorption of oxygen after a certain length of time, but it also yields lignins of higher melting points for the same amount of oxygen absorbed. Thus, the mechanism of lignin oxidation seems to depend on the pH of the lignin solution.

Whether or not lignins of the same melting point, but oxidized at different pH values, differ could not be established, but there is no indication that this is the case. GR-S-containing crumbs, prepared from either lignin under otherwise identical conditions, have the same appearance.

As shown in Figs. 5 and 6, experiments in which the pH was kept constant showed only a slight decrease in the rate of oxygen consumption, even after longer exposure. This would suggest that oxidized lignins, when subjected to further oxidation, could not be expected to show too great a reduction in the rate of oxygen absorption, when compared with lesser or even unoxidized lignin samples. Thus, the possibility of distinguishing between lignins of various degrees of oxidation by this volumetric oxidation method seemed rather slight.

Nevertheless, experiments were carried out to compare the oxygen absorption by unoxidized and oxidized deciduous, as well as coniferous alkali lignins, the pH being allowed to drift. The results are plotted in Fig. 7. The lignin characteristics at the start of the runs and after 20 hr. oxidation are given in Table IV.

As indicated by Fig. 7, both unoxidized deciduous and coniferous alkali lignins absorb oxygen at approximately the same rate, with the same final pH. The oxidized lignins, as was to be expected, took up oxygen somewhat more slowly than the unoxidized samples, but without showing sufficient difference to distinguish lignins of varying degree of oxidation.

TABLE IV

Type of lignin used	Melting point at start, °C.	After 20 hr.	
		Melting point, °C.	% oxygen absorbed
Unoxidized deciduous alkali	168	245	4.9
Oxidized deciduous alkali	349	Not at 360	3.6
Unoxidized coniferous alkali	208	Not at 360	5.0
Oxidized coniferous alkali	Not at 360	Not at 360	3.9

NOTE:—The above reported melting points were determined by the open-tube method.

What apparently happens is that treatment of lignin with oxygen, on the alkaline side, first opens up new acidic groupings in the lignin molecule, but soon starts degrading the molecule more and more, forming low molecular, acidic degradation products, and causing the remaining lignin to assume increasingly lyophilic properties, and eventually completely degrading the remaining lignin skeleton.

Fig. 7 also shows that unoxidized deciduous alkali lignin, when suspended in water and treated with oxygen at 70° C., undergoes only comparatively little oxidation, with an increase in melting point after 20 hr. from 169° C. to only 180° C., and correspondingly low oxygen consumption.

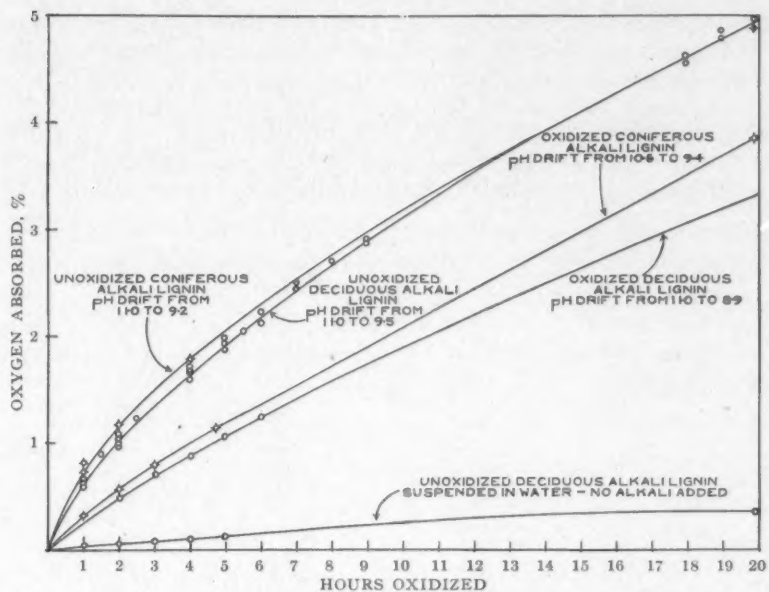


FIG. 7. Oxidation rates for various lignins at 70° C.—pH drift.

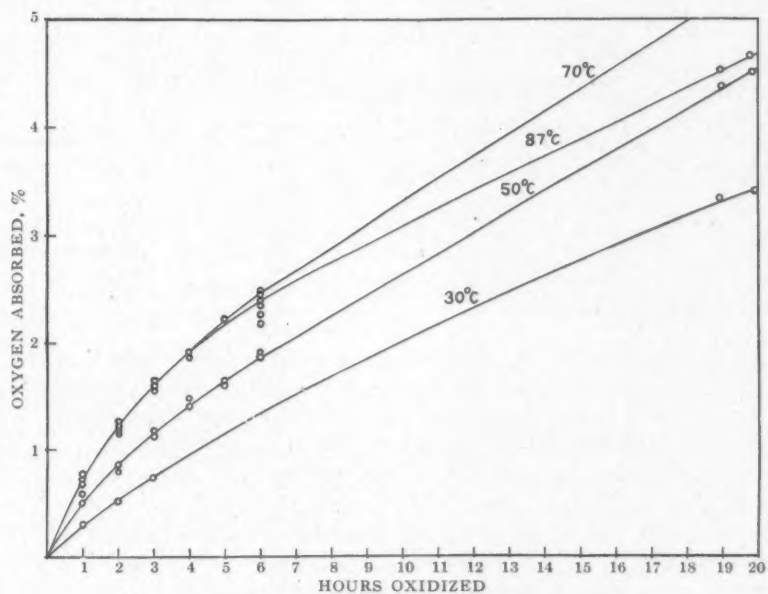


FIG. 8. Oxidation rates at various temperatures—pH drift.

A sample of dry unoxidized deciduous alkali lignin, when subjected to oxygen at 70° C. for 20 hr., showed no measurable oxygen consumption, with an increase in melting point to only 177° C.

(c) *Oxidation Rates at Temperatures Below and Above 70° C.*

It seemed also to be of interest to investigate the rates of oxidation for the same lignin, under otherwise identical conditions, at various temperatures.

Results of experiments of this kind are shown in Fig. 8. At temperatures below as well as above 70° C., the rate of oxidation seems to slow down.

TABLE V  
SUMMARY OF TEST RESULTS

Deciduous alkali lignin type	Oxidation conditions				Filter tests on precip. lignin <sup>1</sup>			Melting points of lignin, ° C.						
	Equip- ment	Hours	Temp., ° C.	pH	Filter time, sec.	Water in cake, % on lignin	Appear- ance of dried cake	Open-tube method		Mercury-covered tube method			Electric stage	
								Shrink.	Melt.	Shrink.	Black	Gas		
Pure	Not oxidized				72	302	Brown, powdery	161	178	150	152	162	165	None
Pure	Roto- Clone	3	66	10.54	123	374	—	181	196	176	180	179	180	1.0%
Pure	Tower	20	81	10.40	280	445	Continual change	205	214	191	193	218	201	1.3%
Crude	Tower	33	70	10.75	375	431		207	217	182	200	217	205	1.5%
Crude	Tower	20	70	10.75	353	438		216	224	191	211	220	212	1.6%
Crude	Tower	20	70	10.85	158	421		214	228	177	210	224	213	1.8%
Pure	Roto- Clone	5	66	10.39	213	419	Black, horny	212	237	197	200	233	217	2.0%
Pure	Roto- Clone	8	66	10.49	118	443		none	289	none	241	305	238	3.5%
Crude	Drum		70	10.40	317	536		none	356	none	226	268	226	5.3%

<sup>1</sup> A 10% solution of the lignin, containing 5.1 gm. m.f. lignin and 5.1 gm. sodium hydroxide, was precipitated at 90° C. to a pH of 2.5. Washing with 250 cc. of water at 90° C.

<sup>2</sup> Derived from Fig. 6, using the "open-tube" method melting points.

<sup>3</sup> Exactly 2.5 gm. dry lignin suspended in 100 cc. of N/100 sodium bicarbonate + N/10 sodium chloride for one hour, and loss in alkalinity of the solution determined.

The decrease caused by the lowering of the reaction temperature is obviously due to the ordinarily observed temperature trend of exothermic reactions, whereas the decrease at temperatures above 70° C. can probably be attributed to the decreased solubility of the oxygen in the lignin solution.

### Conclusions

Although the oxidation range that has been studied is rather small, yield determinations indicate that even in this narrow range considerable amounts of lignin, up to 20%, are degraded to products of acidic character, of sufficiently low molecular weight to evade precipitation by subsequent acidification. This

suggests that more intense oxidation would probably break down the whole of the lignin molecule, as already observed by others, whereas mild oxidation causes primarily the formation of carboxyl groupings, without considerably changing the internal structure of the molecule, as already suggested by Freudenberg. The melting point of the lignin and its lyophilic properties are increased by continued oxidation, and, as already pointed out, these two properties seem to be mainly connected with and possibly responsible for the reinforcing properties in rubber.

A survey of all the data obtained on deciduous alkali lignins of varying

V  
TEST RESULTS

Lignin characteristics						Filter tests on wet precip. lignin GR-S crumb <sup>5</sup>			Test results on batch-oxidized lignins. Coprecipitate with GR-S compounded and cured <sup>6, 7</sup>					
% <sup>2</sup> Oxygen taken up by oxidat.	% Cu <sub>2</sub> O deposit from Fehling soln.	% Iodine consum.	Carb-oxy <sup>1</sup> , milli-equiv./100	% Meth-oxy	% Vis-cos.	Filter time, sec.	Water in cake, % on solids	Filtering considered	Best cure	Tensile, psi.	Elong. %	Modulus 300%	C.P. Mooney	Over-all reinforc.
None	12.05	315	6.48	19.70	4.24	20	74	Good	20	1810	790	411	60	Poor
1.0%	7.55		23.42	19.60	4.58			Good	60	2678	700	677	78	
1.3%	7.32	304	23.29			22	163	Excel.	60	3119	650	900 <sup>8</sup>	84	
1.5%						16	141	Very good	60	3220	680	1005		
1.6%						13	128	Very good	65	3100	650	1090		
1.8%					4.70	15	138	Very good	60	3185	680	1005		
2.0%	4.91		21.22	19.30		21	153	Fair	40	2521	700	700	74	
3.5%	5.52	291	25.48			35	224	Poor	50	2719	730	717	86	Satisfactory
5.3%	6.70		18.10	18.90		42	216	Very poor	70	2521	750	649		

<sup>1</sup> Measured on a 10% solution in cellosolve.

<sup>2</sup> Crumb containing 17 gm. lignin + 34 gm. GR-S, coprecipitated at 90° C.

<sup>3</sup> All lignin-GR-S crumbs were prepared by coprecipitation of mixtures of 10% lignin solution plus 30% GR-S-latex, in the ratio of lignin to GR-S-solids = 1 to 2, at 90° C., by acid and brine.

<sup>7</sup> Strength tests carried out by Research Department of Polymer Corporation Limited, in Sarnia, published with their permission.

degrees of oxidation as well as of their coprecipitates with GR-S latex is given in Table V. The lignins discussed therein are arranged by starting with unoxidized lignin ("Tomlinite") and progressing through medium-oxidized towards overoxidized samples, as indicated by the increase in melting point. The filter tests on the precipitated lignins show the increase in their lyophilic properties resulting from increasing degree of oxidation, as indicated by slower filtering rate and a higher percentage of water content in the filter cake. The appearance of the dried cake also changes gradually, the cake being brown and powdery in the unoxidized lignins, and turning gradually black and horny in the "overoxidized" samples.



Also reported in Table V are the melting points obtained by the three methods, whose interrelation has already been discussed. The technique of oxidation used in the preparation of the lignins described in Table V did not allow a quantitative measurement of the oxygen consumed.

However, volumetric experiments as outlined in the previous section have allowed an estimate of the amount of oxygen taken up by lignin for any given melting point. Thus the appropriate values obtained in this way have been included in Table V under the heading "% Oxygen Taken Up by Oxidation". It appears that an absorption of 1.3 to 2.0% oxygen by the regular "Tomlinite" yields a lignin best suited as a reinforcing agent for GR-S, if coprecipitation is carried out between 80° and 90° C., and if the solutions are not too dilute.

Also shown in Table V are other lignin characteristics, such as copper number, iodine value, carboxyl number, methoxyl content, and viscosity in cellosolve, the significance of which has already been discussed.

The wet crumbs which were coprecipitated in a ratio of 2:1 at 80° to 90° C. from mixtures of 30% latex with 10% lignins of varying degrees of oxidation behave similarly to the corresponding lignins if coprecipitated under identical conditions in so far as filter times and moisture contents are concerned. In general the higher the degree of oxidation, the slower is the filtering rate and the higher is the water content in the wet crumb.

These lignin-containing crumbs were dried, compounded, cured, and tested in the manner previously described (5). The results obtained are shown in Table V and, assuming identical coprecipitation conditions, indicate poor reinforcement by unoxidized and very slightly oxidized lignins and good reinforcement by medium oxidized lignins. The reinforcement again becomes poorer for "overoxidized" samples, which are also harder to handle in milling and compounding.

### Acknowledgment

Thanks are due to Mr. Rolland Hebert, who carried out most of the volumetric oxidations, and to Polymer Corporation Ltd. in Sarnia, particularly to Mr. W. H. Watson, for permission to include in this paper some of the testing results on lignin reinforced rubbers. The permission by Mr. G. H. Tomlinson, Vice-President of Howard Smith Paper Mills Limited, to publish this paper is also gratefully acknowledged.

### References

1. BENNETT, E. *Soil Sci.* 55 : 427. 1943.
2. FISCHER, F., et al. *Abhandl. Kohle*, 5 : 221. 1922; 6 : 1. 1923; etc.
3. POWEL, W. J. and WHITTAKER, H. *J. Chem. Soc.* 125 : 357. 1924.
4. RAFF, R. A. V. *Can. Chem. Proc. Inds.* 33 : 35. 1949.
5. RAFF, R. A. V., TOMLINSON II, G. H., DAVIES, T. L., and WATSON, W. H. *Rubber Age* (N.Y.), 64 : 197. 1948.
6. SCHUERCH, C. Quarterly Report of the Pulp and Paper Research Institute of Canada, September to November, 1947.
7. WALDE, A. W. and HIXON, R. M. *J. Am. Chem. Soc.* 56 : 2656. 1934.
8. WILSON, K. *Svensk Papperstidn.* 51 : 45. 1948.

## RATION BISCUITS

### V. EFFECTS OF KIND AND CONCENTRATION OF VARIOUS CONSTITUENTS ON KEEPING QUALITY<sup>1</sup>

BY H. J. LIPS<sup>2</sup>, J. B. MARSHALL<sup>3</sup>, W. HAROLD WHITE<sup>4</sup>,  
AND G. A. GRANT<sup>5</sup>

#### Abstract

Ration-type biscuits commercially prepared according to a basic formula, with increasing levels of supplementary ingredients tested one at a time, gave the following results for flavor tests and chemical analyses when stored in sealed cans at 110° F. for periods up to 88 weeks: flavor score was improved by sugar and impaired by skim milk powder and salt; peroxide oxygen value of extracted fat was increased by salt and decreased by defatted soybean flour; fluorescence of a potassium chloride extract of defatted biscuit was increased by defatted soybean flour, baking soda, skim milk powder, malt, and salt, and decreased by sugar; pH of the potassium chloride extract was increased by defatted soybean flour and soda, and decreased by skim milk powder and malt. Shortening stability was a limiting factor in determining the relative effects of the other components on biscuit keeping quality. Biscuits containing all the supplementary materials had good keeping quality when a stable vegetable shortening was used.

#### Introduction

Previous papers on simple formula ration biscuits from these laboratories described effects of shortening, moisture, and a number of protein supplements on keeping quality (4, 6, 8, 11). However, the stability of ration biscuits might be influenced by the kind and concentration of any constituent, and by various interactions between added materials. Other work has indicated the stabilizing action of molasses and spices (9), sugar (3, 7) and wheat oil (12) in crackers; and the deleterious action of salt in processed cereal flakes (13). This paper describes experiments to determine the effect of some of the more commonly used ingredients, singly and in combination, on the keeping quality of stored biscuit material.

#### Materials and Methods

Four series of biscuits were commercially prepared according to a basic formula, with extra materials added in concentrations expressed as percentages of the amount of soft wheat flour in the basic formula. Two types of shortening, animal-vegetable and hydrogenated all-vegetable, were used. The basic formula was 50 lb. soft wheat flour, 5 lb. shortening, 6 oz. baking soda, and water as required.

<sup>1</sup> Manuscript received July 28, 1949.

Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as Paper No. 237 of the Canadian Committee on Food Preservation and as N.R.C. No. 2015.

<sup>2</sup> Biochemist, Fats and Oils Laboratory.

<sup>3</sup> Biologist, Food Investigations.

<sup>4</sup> Formerly Biochemist, Food Investigations; now Chemist, Imperial Oil Co., Ltd., Sarnia.

<sup>5</sup> Formerly Technical Officer, Food Investigations; now Technical Officer, Defence Research Laboratories, Ottawa.

In Series I (animal-vegetable shortening No. 1) whole wheat flour and defatted soybean flour were each tested in three concentrations as *substitutes* for part of the soft wheat flour, and baking soda was tried at five levels (Table I). In Series II (hydrogenated vegetable shortening No. 1) skim milk powder, malt, salt, and sugar were tested as *additions* to the basic formula in the varying concentrations shown in Table II, and the amount of shortening adjusted slightly when necessary to give a satisfactory mix. The same materials used in Series I and II were used in Series III (animal-vegetable shortening No. 2), at single concentrations only (the median values of the concentration ranges in the first two series), in order to determine the relative effects of the different supplements (Table III).

As it would have been laborious to determine the results of simultaneous variation of a large number of constituents at several concentrations of each, Series IV (hydrogenated vegetable shortening No. 2) was designed to test the effect of *omitting*, one at a time, whole wheat flour, defatted soybean flour, skim milk powder, malt, salt, and sugar from a complete formula (Table IV). Whole wheat flour (40%) was *substituted for part of* the soft wheat flour in the basic formula, and soybean flour (20%), skim milk powder (20%), malt (6%), salt (2.25%), and sugar (20%) were *added* to the basic formula. It was necessary to adjust these amounts slightly as each supplementary constituent was omitted in turn, but the total of soft wheat and whole wheat flour was maintained at 50 lb. in each of the batches. The quantity of shortening was increased from 5 lb. to 8 lb.

Preliminary determinations of fat and moisture (4) and of nitrogen (1) showed that the desired proportions had been satisfactorily approximated in all the preparations. Moisture contents were all between 6 and 9%, a range unlikely to cause stability differences (8). The biscuits were stored in sealed No. 1 cans at 110° F., and sampled at eight-week intervals for periods up to 88 weeks. Deterioration was assessed by peroxide oxygen, pH, and fluorescence determinations, and by flavor scores, according to methods previously described (4, 8). The results of Series I and II were examined by fitting regression lines to the data for each variable, and by analyses of variance.

## Results

For all series of biscuits, the flavor scores and peroxide oxygen values obtained at different storage times were rather irregular, whereas pH and fluorescence measurements were more consistent. Peroxide values tended to fall after reaching a maximum, while fluorescence values tended to level off after an early rise. In general, however, peroxide oxygen and fluorescence values rose and pH values fell as the flavor of the biscuit materials deteriorated, but the magnitude and speed of these changes varied considerably with the kind and concentration of the supplementary ingredients. Graphical pre-

sentations of similar changes in biscuit material were made in earlier papers (4, 6, 8, 11). Mean values over all samplings for the different measurements are shown in Tables I to IV.

Biscuits of Series I and III (animal-vegetable shortenings) remained acceptable for 16 to 40 weeks, and those of Series II and IV (hydrogenated vegetable shortenings) remained acceptable for 72 to 88+ weeks.

#### *Series I and II*

To determine the effect of increasing the amount of each of the different materials tested, irrespective of storage time, the data for each group of

TABLE I  
MEAN VALUES OVER ALL SAMPLINGS FOR 24 WEEKS FOR KEEPING QUALITY  
MEASUREMENTS ON BISCUITS STORED AT 110° F.  
(Series I, animal-vegetable shortening No. 1)

Supplementary ingredient, %	Flavor score, 0-10 basis	Peroxide value, ml. of 0.002 <i>N</i> thiosulphate per gm. of extracted fat	pH of potassium chloride extract of defatted biscuit	Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units
Whole wheat flour 10	7.6	3	6.8	39
25	7.6	2	6.9	37
40	7.4	4	6.7	38
Defatted soybean flour 4	7.1	12	6.8	44
12	7.3	8	7.0	48
20	7.3	5	7.0	51
Baking soda* 0.25	6.0	82	6.5	23
0.50	6.2	94	6.5	36
0.75	6.4	18	6.8	42
1.00	6.1	76	6.8	43
1.25	6.1	39	7.7	48

\*These values represent total amounts of soda in the biscuit.

constituents were first examined separately. Only three components gave significant regression coefficients for flavor change with change in concentration (Table V). Increasing the amount of skim milk powder or salt was detrimental to flavor score, while additional sugar tended slightly to improve it. Additional amounts of soda tended to depress flavor at 8 and 16 weeks' storage and to increase it at 24 weeks, but showed no effect at the other sampling periods. Whole wheat flour, defatted soybean flour, and malt had no demonstrable concentration effect on flavor.

On the average, peroxide oxygen value decreased with additional amounts of soybean flour, and increased with additional amounts of salt, but was insensitive to changes in quantity of the other ingredients.

TABLE II  
MEAN VALUES OVER ALL SAMPLINGS FOR 88 WEEKS FOR KEEPING QUALITY  
MEASUREMENTS ON BISCUITS STORED AT 110° F.  
(Series II, hydrogenated vegetable shortening No. 1)

Supplementary ingredient, %	Flavor score, 0-10 basis	Peroxide value, ml. of 0.002 N thiosulphate per gm. of extracted fat	pH of potassium chloride extract of defatted biscuit	Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units
Skim milk powder 4	6.1	2	6.1	20
12	5.6	2	6.0	33
20	5.2	2	6.0	43
Malt 2	6.8	2	5.9	27
4	6.8	2	5.7	32
6	6.9	2	5.7	39
Salt 0.75	6.9	3	5.8	20
1.50	6.6	3	5.8	19
2.25	6.6	5	5.8	24
Sugar 4	7.4	2	5.9	17
12	7.5	1	6.0	13
20	7.6	2	5.8	13

pH tended to diminish with additional skim milk powder and malt, and to increase with additional soda (as expected) and soybean flour. It was unaffected by variation in amounts of whole wheat flour, salt, and sugar.

Fluorescence was increased in varying degree by the incorporation of additional amounts of soybean flour, soda, skim milk powder, malt, and salt; but was reduced by added sugar. Varying the amount of whole wheat flour produced no significant change.

TABLE III  
MEAN VALUES OVER ALL SAMPLINGS FOR 24 WEEKS FOR KEEPING QUALITY  
MEASUREMENTS ON BISCUITS STORED AT 110° F.  
(Series III, animal-vegetable shortening No. 2)

Supplementary ingredient, %	Flavor score, 0-10 basis	Peroxide value, ml. of 0.002 N thiosulphate per gm. of extracted fat	pH of potassium chloride extract of defatted biscuit	Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units
Whole wheat flour 25	6.8	11	6.4	48
Defatted soybean flour 12	6.6	8	6.8	41
Baking soda 0.75*	6.5	4	6.8	29
Skim milk powder 12	6.9	2	6.6	41
Malt 4	6.6	2	6.5	52
Salt 1.5	6.2	14	6.5	27
Sugar 12	6.5	14	6.8	25

\*This value represents the total amount of soda in the biscuit.



TABLE IV

MEAN VALUES OVER ALL SAMPLINGS FOR 88 WEEKS FOR KEEPING QUALITY  
MEASUREMENTS ON BISCUITS STORED AT 110° F.  
(Series IV, hydrogenated vegetable shortening No. 2)

Supplementary ingredient omitted from complete formula	Flavor score, 0-10 basis	Peroxide value, ml. of 0.002 N thiosulphate per gm. of extracted fat	pH of potassium chloride extract of defatted biscuit	Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units
None (complete)	6.4	2	5.9	91
Whole wheat flour	6.5	2	6.1	77
Defatted soybean flour	7.1	2	6.3	52
Skim milk powder	7.0	4	6.5	41
Malt	6.4	2	6.1	62
Salt	6.7	2	6.0	85
Sugar	6.2	2	5.9	89

For those constituents showing no effects related to concentration, the question remained whether they nevertheless modified the characteristics of all biscuits in which they were present, regardless of amount. Suitable comparisons could be made only among biscuit groups prepared with the same shortening. Analyses of variance of the comparative flavor scores for whole wheat and soybean flour biscuits demonstrated a more rapid deterioration of

TABLE V

AVERAGE CHANGES IN MEASUREMENTS OF KEEPING QUALITY OF  
BISCUITS STORED AT 110° F. FOR EACH PER CENT  
INCREASE IN CONSTITUENT CONCENTRATION  
(Series I and II)

Keeping quality measurement	Constituent	Regression coefficients,* representing change in keeping quality measurements for each per cent increase in constituent concentration
Flavor score, 0-10 basis	Skim milk powder	— .06
	Salt	— .21
	Sugar	.01
Peroxide oxygen value, ml. of 0.002 N thiosulphate per gm. of extracted fat	Defatted soybean flour	— .42
	Salt	2.33
pH of potassium chloride extract of defatted biscuit**	Defatted soybean flour	.02
	Baking soda	.86
	Skim milk powder	— .01
	Malt	— .02
Fluorescence of potassium chloride extract of defatted biscuit, Coleman photofluorometer units	Defatted soybean flour	.44
	Baking soda	19.53
	Skim milk powder	1.41
	Malt	3.06
	Salt	2.61
	Sugar	— .26

\*Only statistically significant coefficients (5% level) presented.

\*\*As pH values are logarithmic, changes of the same numerical magnitude in different pH ranges are not equivalent.

the latter during storage. Peroxide oxygen value was higher at the earlier sampling times in the sodium bicarbonate biscuits than in those containing whole wheat flour; it was significantly lower at 40 to 56 weeks in biscuits containing sugar than in those having skim milk powder or malt; but these differences were not evident at other sampling times for the same materials. Biscuits containing salt or sugar did not differ in pH changes.

### *Series III*

Measurements for Series III biscuits (animal-vegetable shortening), shown in Table III, indicated a somewhat different relative effect of supplementary constituents than did the measurements for the corresponding batches of Series I and Series II biscuits. Whole wheat flour and defatted soybean flour biscuits were only slightly superior to the soda batch in flavor, and had higher peroxide and fluorescence values. In the presence of the animal-vegetable shortening, sugar appeared to have little effect either in improving flavor or preventing formation of peroxides in the fat fraction. Skim milk powder appeared to have a stabilizing effect, as opposed to its undesirable action in Series II with the more stable (vegetable) shortening. However, the action of salt was deleterious, as before.

### *Series IV*

The results for the series in which individual constituents were omitted, one at a time, from a complete formula (Table IV) showed that these samples differed very little in keeping quality, all remaining acceptable for 80 to 88 weeks at the storage temperature of 110° F. The sample without skim milk powder appeared to differ most widely from all others in the group, having relatively good flavor, high pH, and low fluorescence but high peroxide value. The omission of defatted soybean flour also appeared to improve the flavor of the biscuit material.

## **Discussion**

A variety of effects due to variations in constituents is possible in biscuits, and some of those described have apparently not been reported heretofore. The improvement of flavor with increasing amounts of sugar could be expected, since sugar at high concentrations functions as an antioxidant for fats (3, 7) and its taste can serve to mask unpleasant flavors. Soda may improve flavor and maintain a desirable pH by neutralizing acidic products of fat deterioration, but an excess imparts a characteristic, unpleasant taste. The use of higher alkali concentrations also causes more gasification, which allows coloring and scorching to take place more easily during baking, and scorching leads to a decrease in keeping quality (12). The sugars in malt and skim milk powder should function as stabilizers, but the action of the malt and milk powder is no doubt complicated by their content of protein and other materials. The action of salt in accelerating rancidity may be due to the presence of other chlorides as impurities (5). Whole wheat flour should function as a better stabilizer than soft wheat flour because of its greater

content of natural antioxidant material. This is in line with the observation that the addition of starch to soften a flour gives poorer biscuit keeping quality (9). Full-fat soybean flour is said to be an effective antioxidant, but this property may be diminished when the flour is defatted (10). However, flour prepared from extracted soybean meal stabilized both dry pastry mixes and baked pastry (2).

It should be noted that the poor stability of the shortening used in the whole wheat flour, soybean flour, and soda groups of Series I may have influenced the results obtained with varying concentrations of these materials. The *relative* effects of different added materials also appeared to depend on the type of shortening used. For example, skim milk powder, which improved biscuits prepared with animal-vegetable shortening, appeared to have the opposite effect in the presence of the more stable hydrogenated vegetable shortening. The data support earlier evidence (6) that shortening stability is a limiting factor in biscuit storage life and suggest that biscuits of good keeping quality can be prepared containing any of the supplementary materials described, if a stable vegetable shortening is used.

The observed variation in the objective measurements with nature and concentration of the supplementary ingredients emphasizes the importance of supporting these objective estimates of quality with palatability tests.

### Acknowledgments

The authors wish to thank Dr. J. W. Hopkins for help with the statistical phases of the work, and Miss J. R. Lewis and Mrs. W. I. Illman for technical assistance.

### References

1. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. Official and tentative methods of analysis. 5th ed. A.O.A.C. Washington, D.C. 1940.
2. BAKER, D. S. The antioxidant effect of edible flours derived from oil press cakes in certain fat-containing food mixtures. Unpublished Thesis (M.Sc.). Oregon State College. 1948.
3. BOHN, R. M. and OLSON, R. S. *Oil & Soap*, 11 : 210, 218. 1934.
4. GRANT, G. A., MARSHALL, J. B., and WHITE, W. H. *Can. J. Research*, F, 23 : 123-131. 1945.
5. HILLS, G. L. and CONOCHIE, J. *J. Council Sci. Ind. Research*, 18 : 355-365. 1946.
6. LIPS, H. J., CROWSON, N. C., and WHITE, W. H. *Can. J. Research*, F, 25 : 51-62. 1947.
7. MCKINNEY, R. H. and BAILEY, A. E. *Oil & Soap*, 18 : 147-148. 1941.
8. MARSHALL, J. B., GRANT, G. A., and WHITE, W. H. *Can. J. Research*, F, 23 : 286-294. 1945.
9. MAVEETY, D. J. *Oil & Soap*, 23 : 25-27. 1946.
10. MUSER, S. *Food Inds.* 7 : 167, 329. 1935.
11. PEARCE, J. A. and MARSHALL, J. B. *Can. J. Research*, F, 23 : 22-38. 1945.
12. TRIEBOLD, H. O. *Oil & Soap*, 22 : 334-336. 1945.
13. WILDER, H. K. and LINDOW, C. W. U.S. Patent No. 2,093,260. 1937.

## THE ADSORPTION OF SODIUM MYRISTATE BY CARBON BLACK<sup>1</sup>

BY MARGUERITE A. READE,<sup>2</sup> A. S. WEATHERBURN,<sup>2</sup> AND C. H. BAYLEY<sup>2</sup>

### Abstract

The adsorption of sodium myristate from 0.1% aqueous solution by a series of carbon blacks and an activated charcoal has been measured at 70° C. In every case a preferential adsorption of fatty acid was observed. The extent of adsorption of both the fatty acid and alkali components of the soap increased with decreasing particle size, i.e., with increasing surface area, of the carbons. The adsorption by activated charcoal was considerably higher than that obtained with even the finest of the carbon blacks.

During the course of studies in the field of detergency currently in progress in these laboratories, it became of interest to investigate the adsorption of soap on carbonaceous materials used as fiber-soiling media. A previous paper (3) gives data relating to the adsorption of various pure soaps on one carbon (standard Micronex) which may be regarded as typical of the carbons employed in detergency studies. The present paper gives data relating to the adsorption of one soap by a range of carbon blacks, differing in physical properties and method of manufacture. The results indicate that the conclusions reached with respect to the selective adsorption of fatty acid by Micronex are not specific for that carbon, but are applicable to carbon blacks in general.

### Experimental

Sodium myristate that had been prepared for the previous work on the adsorption of soaps by Micronex (3) was used throughout the present work.

The carbon blacks studied are listed in Table I, the data for mean particle diameter, surface area, and structure index being obtained from manufacturers' literature (1, 2, 4).

The concept of "structure" in carbon blacks has been discussed by Sweitzer and Goodrich (2) and by Weigand (4). For many carbon blacks, certain properties, such as bulk density, sedimentation volume, liquid adsorption, and effect on the physical properties of rubber mixes, may be correlated with particle size. Such carbons are said to have a normal structure. Certain carbons, however, deviate from the normal in that they give values for the above properties that are either higher or lower than those that would be predicted from their particle sizes. "Structure index" is defined as the degree of oil adsorption (determined under standardized conditions) compared with the oil adsorption of a normal carbon of the same particle size taken as 100.

<sup>1</sup> Manuscript received July 7, 1949.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 2003.

The present work was part of a research program financed by the Canadian Research Institute of Launderers and Cleaners, to whom we wish to express our grateful acknowledgment.

<sup>2</sup> Chemist.

TABLE I  
 ADSORPTION OF SODIUM MYRISTATE BY VARIOUS CARBONS

Carbon	Mean particle diameter, $m\mu$	Specific surface, $m^2/gm.^1$	Structure index	Adsorption, millimoles/gm. carbon		
				No. of determinations	Fatty acid	Alkali
Neo Spectra II	12.7	205	100	12	$0.662 \pm 0.009$	$0.603 \pm 0.012$
Superba	16	163	100	4	$0.468 \pm 0.004$	$0.427 \pm 0.005$
Exceisor	20	134	100	8	$0.329 \pm 0.003$	$0.280 \pm 0.003$
Standard Micronex	28	95	100	4	$0.220 \pm 0.005$	$0.150 \pm 0.002$
Statex B	34	75	100	8	$0.180 \pm 0.004$	$0.104 \pm 0.003$
Acetylene black	43	65	300	8	$0.163 \pm 0.004$	$0.111 \pm 0.003$
P-33	74	37	60	12	$0.103 \pm 0.007$	$0.058 \pm 0.002$
Lampblack	97	23	200	20	$0.122 \pm 0.006$	$0.086 \pm 0.001$
Cocoanut shell charcoal	—	—	—	4	$0.980 \pm 0.002$	$0.466 \pm 0.005$

<sup>1</sup>Recalculated from manufacturers' data, which is given in acres per lb.

For purpose of comparison with the carbon blacks, adsorption measurements were also carried out on an activated cocoanut shell charcoal. This material had been steam activated, and prior to use was ball milled to pass a 200 mesh screen. The maximum particle diameter was thus about  $74\mu$ , but the available surface area was undoubtedly much larger than this diameter would indicate, owing to the porosity of the material.

The method of determining adsorption has been described previously (3). It consists essentially of shaking a weighed amount of carbon with soap solution, filtering off the carbon, and determining the fatty acid and alkali content of the filtrate.

Preliminary attempts were made to use sodium stearate as the adsorbate, since it had been shown previously that this soap is highly adsorbed by Micronex (3). However, it was found that for many of the carbons the suspending and/or solubilizing power of sodium stearate was so great that clear filtrates could not be obtained. This difficulty was eliminated when sodium myristate was substituted as the adsorbate, and consequently this soap was used throughout the present work.

The adsorption of sodium myristate from 0.1% aqueous solution at  $70^\circ C$ . was determined for each of the carbons. Prior to the adsorption measurements the carbons were tested for extractable acid or alkali by shaking with boiled out distilled water in a manner similar to that employed in the adsorption measurements, filtering off the carbon, and determining the acid or alkali content of the filtrate. No titratable amount of acid or alkali was obtained from any of the carbon blacks, but the cocoanut shell charcoal gave an amount of alkali equivalent to 0.149 millimole per gram. The value for the adsorption of alkali from soap solution was therefore low by this amount, and was corrected by adding 0.149 to the apparent adsorption obtained. The results are given in Table I and Fig. 1.



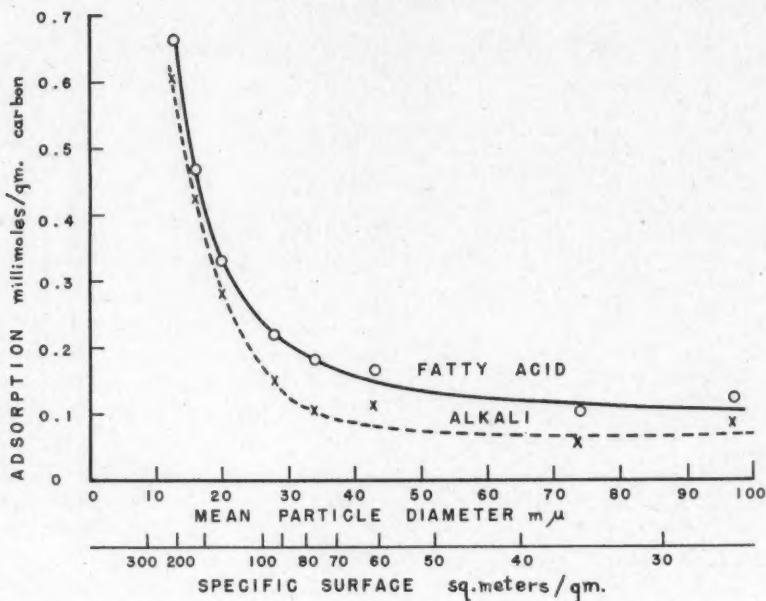


FIG. 1.

### Discussion

In every case the adsorption of the fatty acid component of the soap was greater than that of the alkali component. This is in agreement with data previously obtained for Micronex (3), and indicates that this property is not specific for Micronex but is characteristic of carbonaceous materials in general.

The adsorption of both fatty acid and alkali increases in a regular manner as the particle diameter becomes smaller, i.e., as the surface area becomes greater. It is interesting to note that the adsorption of both components of the soap by the high structure carbons acetylene black and lampblack falls above the curve for the normal structure carbons, whereas the adsorption by the low structure carbon P-33 falls below it. This is in accord with the foregoing discussion of carbon structure.

The adsorption of soap by coconut shell charcoal was considerably higher than that obtained with any of the carbon blacks. This may be attributed to the porous nature of the material resulting in a very large specific surface.

### References

1. COLUMBIAN CARBON COMPANY. Columbian colloidal carbons, Vol. 3, Columbian Carbon Company, New York. 1942.
2. SWEITZER, C. W. and GOODRICH, W. C. Rubber Age (N.Y.), 55 : 469-478. 1944.
3. WEATHERBURN, A. S., ROSE, G. R. F., and BAYLEY, C. H. Can. J. Research, F, 27 : 179-193. 1949.
4. WEIGAND, W. B. Can. Chem. Process Inds. 28 : 151-162, 213. 1944.

## THE "BROWNING REACTION" IN DRIED MILK POWDER<sup>1</sup>

By J. B. MOSTER<sup>2</sup> AND R. A. CHAPMAN<sup>3</sup>

### Abstract

Heated and stored dried milk powders showed a marked loss of amino nitrogen as determined by the Van Slyke volumetric method, but no loss was observed when the formol titration was used. Titration curves of the powders suggested a mechanism for the protein-sugar condensation. The heating of synthetic mixtures of amino acids and lactose resulted in intense browning, accompanied by a loss of amino nitrogen when a large excess of lactose was employed but no loss occurred when equal parts of sugar and amino acid were present.

### Introduction

The technique of preserving food by drying has improved rapidly during the past decade. However, even modern processing methods do not prevent deterioration of dehydrated foods for indefinite periods. This instability has been particularly apparent under the drastic conditions encountered by the armed services and consequently a considerable amount of research is being conducted in this field. The present investigation was undertaken to study the chemical processes involved in the "browning reaction" in dried milk powder, since an understanding of the fundamental nature of the reaction should be of value in preventing its occurrence.

Kass and Palmer (3) and Joslyn (2) have reviewed the "browning reaction" in food products. These papers revealed that some investigators have found evidence of the formation of a protein-sugar complex. Other workers have been unable to detect any decrease in amino nitrogen after browning had occurred, and they have concluded that the reaction involves a protein-catalyzed degradation of the sugar followed by a physical adsorption of the breakdown products on the protein.

Lea and White (5) have recently reported a loss of amino nitrogen during storage of dried milk powder as determined by both the Van Slyke volumetric and the formol titration methods. The decrease was significantly greater when the Van Slyke technique was employed. These workers have suggested that the basic character of the amino group may not be sufficiently weakened by the initial reaction it undergoes during deterioration of the powder to prevent partial titration under the conditions of the formol estimations.

<sup>1</sup> Manuscript received July 9, 1949.

Contribution from the Department of Chemistry, Faculty of Agriculture (McGill University) Macdonald College, Que. Macdonald College Journal Series No. 255. This paper reports research undertaken in co-operation with the Quartermaster Food and Container Institute for the Armed Forces (United States), and has been assigned No. 263 in the series of papers approved for publication. The views or conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or indorsement of the Department of the Army.

<sup>2</sup> Swift Canadian Company Research Fellow. Present address: Department of Agricultural Chemistry, Purdue University, Lafayette, Indiana, U.S.A.

<sup>3</sup> Assistant Professor of Chemistry. Present address: Food and Drugs Division, Department of National Health and Welfare, Ottawa, Canada.

In general the results obtained in this investigation confirm those of Lea (4) and Lea and White (5). In addition, information has been obtained, which, it is believed, will further elucidate the "browning reaction".

### Experimental

Amino nitrogen was determined by the Van Slyke volumetric and the formol titration methods. A 30 min. shaking period was employed, for the Van Slyke method. Milk powders, reconstituted in distilled water, tended to foam over in the gas burette of the Van Slyke apparatus when treated with glacial acetic acid and sodium nitrite. Excessive foaming could be prevented by placing the reconstituted milk in a boiling water bath and agitating it vigorously with a mechanical stirrer for 15 min. This mild heating treatment did not result in any noticeable browning of the reconstituted milk, nor was there any measurable change in the formol titration values or in the dissociation properties. Ten grams of milk powder was reconstituted in about 40 ml. of distilled water and, after cooling, the volume was made up to 50 ml. Amino nitrogen was determined on 10 ml. aliquots.

Levy (6) has reported that maximum accuracy in the formol titration of amino acids was obtained when neutralized formaldehyde was employed and no correction was made for a blank. It was recommended that the concentration of formaldehyde should be between 6% and 9% at the end of the titration. These recommendations were adopted in the present investigation. The titration was carried out between pH 7.0 and pH 9.1.

Measurements of pH were made with a Beckman pH meter (Model G), equipped with a standard glass electrode assembly. The following procedure was employed. Ten grams of milk powder was reconstituted in 200 ml. of distilled water, and the pH was adjusted to 7. Sixty milliliters of neutralized 40% formaldehyde was added and the solution was titrated at 25° C. to pH 9.1, with 0.1 *N* sodium hydroxide. The solution was vigorously agitated with a mechanical stirrer while the pH readings were being made. The rate of addition of the standard solution and a titration period of seven minutes were carefully controlled for all determinations.

Samples of fresh, heated, and very stale whole milk powders were examined. The heated sample was prepared by heating a fresh milk powder at 100° C. for two days. The loss of volatile substances during the heating of the powder was determined, and an amount of the heated samples equivalent to 10 gm. of the fresh sample was employed for the amino nitrogen and the titration curve experiments. Only one suitable stale sample of milk powder was available at the time of this investigation. This sample had been stored for four years in an unheated room in a container with a slip-on cover. The results of the amino nitrogen determinations are presented in Table I.

In the titration curve experiments, the milk powders were titrated at 25° C. between pH 6 and 11.3. The pH readings were taken with the same

TABLE I  
THE FREE AMINO NITROGEN CONTENT OF FRESH, HEATED, AND  
STORED SPRAY-DRIED WHOLE MILK POWDERS

Sample	Mgm. of amino N per gm. of milk powder*	
	Van Slyke	Formol
Fresh	2.93	3.64
Heated	1.73	3.71
Stale	1.65	3.53

\*Dry weight.

pH meter used for the formol titration. For all readings above pH 9, a Beckman "Type E" glass electrode was used.

In order to minimize the error caused by changes in ionic strength during titration, sufficient sodium chloride was added to the reconstituted milk to make the solution 1 *N*. The solution was titrated with 0.1 *N* sodium hydroxide to which had been added sufficient sodium chloride to make it 1 *N* with respect to the sodium ion. It was assumed that the contribution of the milk powder to the ionic strength of the reconstituted solution would not be appreciable. Since only 10 gm. was reconstituted in a liter of distilled water, the effect on the ionic strength of diluting this volume with a 100 ml. of the standard solution would be negligible.

The titration of milk powder was carried out in the following manner. Ten grams of the powder was reconstituted in 500 ml. of distilled water, 58.5 gm. of sodium chloride was added, and the volume was made up to 1 liter. The electrode was then standardized and the solutions, in turn, were adjusted to pH 6, using 1 *N* hydrochloric acid. An aliquot of standard alkali was added to each of the samples and the pH of each was taken. The electrode was then restandardized, and, if any change in asymmetry potential had occurred, the meter was readjusted and the pH of the solutions was taken again. This procedure was continued until the titrations were complete. Samples being compared were always titrated at the same time.

A blank solution, consisting of 1 liter of 1 *N* sodium chloride was titrated in a similar manner and at the same time as the milk powder samples. The volume of standard solution required to bring the blank to a particular pH was subtracted from the volume required to bring the milk powder solution to the same pH. The volumes thus obtained were then plotted against the pH values. The accuracy obtained by this method became progressively smaller as the alkalinity of the solution increased. Thus, it was found that above pH 11 it was not possible to obtain reliable results. However, this has not proved to be a serious hindrance, since a satisfactory study could be made on the portion of the curves below pH 11.

The titration curves of the milk powders are presented in Fig. 1. A number of other fresh and heated samples have been titrated, and in all cases similar results were obtained.

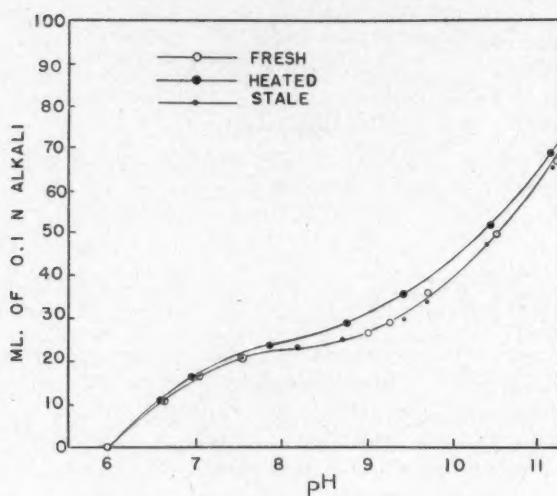


FIG. 1. Titration curves of fresh, heated and stale milk powders (10 gm. of milk powder in 1 l. of water used in each case).

Experiments, similar to those carried out on the milk powders, were also made on simple amino acid-lactose systems. At the time that this research project was terminated, this portion of the investigation had not been satisfactorily completed. Therefore only certain parts of these experiments are being reported.

Synthetic mixtures of glycine and lactose, and lysine monohydrochloride and lactose were made up in two concentrations: (1) 1 part by weight of the amino acid to 13 parts of the sugar, and (2) equal parts of each constituent. These mixtures were prepared and treated as described in Table II. In all

TABLE II  
LOSS OF AMINO NITROGEN IN SYNTHETIC MIXTURES OF AMINO ACIDS  
AND LACTOSE

Preparation*	Treatment		% loss of amino nitrogen			
			Glycine-lactose ratio by weight		Lysine HCl-lactose ratio by weight	
	Temp., °C.	Time	1 : 13	1 : 1	1 : 13	1 : 1
(1)	130	2 days	20.3	0	—	—
(2)	100	7 hours	39.2	0	28.8	0
(3)	115	2 days	18.8	0	—	—

\*(1) Components ground together.

(2) Components ground together and placed in a closed vessel over a saturated solution of sodium nitrate.

(3) Components mixed, dissolved in distilled water, and dried from the frozen state.



cases, control samples of amino acid alone and lactose alone were treated in a manner similar to the treatment of the synthetic mixtures. No significant browning occurred in the controls. In the mixtures, treatment with moist heat produced the darkest samples, the lyophilized samples were intermediate, and the mixtures prepared by the first method were the least discolored.

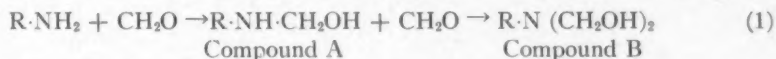
After being treated, the mixtures were dissolved in distilled water, and suitable aliquots were taken for Van Slyke amino nitrogen determinations. A five minute shaking period was used for the glycine mixtures and a 20 min. period for the lysine mixtures. The results are presented in Table II.

### Discussion

It is seen from the results in Table I that the amino nitrogen of the fresh sample, as determined by the volumetric technique, is about 20% lower than the value obtained by the formol titration. This difference may have been the result of an incomplete reaction between nitrous acid and the milk protein, but, more likely, was due to the fact that substances or groups, other than amino groups, were titrated in the formol titration.

The results also show that the Van Slyke volumetric technique gave much lower values for the stale and heated milk powders than for the fresh sample. However, corresponding differences were not obtained when the formol titration method was employed.

An explanation for this difference may be obtained on examination of the curves in Fig. 1. It is seen that the heated powder has more titratable groups between pH 6 and 9.25. Most of these groups would be titrated in the formol titration. If the number of amino groups lost during browning equalled the number of new titratable groups formed, then the formol titration would not indicate any loss of amino nitrogen. The results described may be explained by assuming that the "browning reaction" involves a condensation of the free amino groups of the milk protein with either lactose or decomposition products of lactose, to form a compound containing a secondary or tertiary amino group. The mechanism of such a condensation may be similar to the generally accepted mechanism for the reaction between formaldehyde and amino acids. This reaction, proposed by Balson and Lawson (1) and Levy and Silberman (7), is represented by the following equation:



It is usually considered that the majority of the free amino groups of milk protein are  $\epsilon$ -amino groups of lysine. The  $pK'$  value of this group is 10.5. By the mechanism suggested, for every  $\epsilon$ -amino group reacting, a less basic group would be formed. This would account for the additional titratable groups observed between pH 6 and 9.25 in the heated milk powder.

The dissociation properties of the condensation products corresponding to compounds A and B in Equation (1), would depend on the number, nature, and size of the groups that have replaced hydrogen on the nitrogen atom. Therefore, by the proposed reaction or by a reaction similar to it, it would seem possible to form a compound that would possess the same dissociation properties as the original  $\epsilon$ -amino group. For this reason, the fact that the titration curves of the fresh and stale\* powders are similar does not necessarily discredit the suggested mechanism.

The results in Table II show the effect of sugar concentration on the sugar-protein condensation. It is seen that browning can occur with or without any loss of amino nitrogen. Variations in the concentration of constituents, and in other simple conditions, are probably the causes of many of the discrepancies that have occurred concerning the loss of amino nitrogen during browning of food products.

### Acknowledgments

The authors wish to thank Dr. R. H. Common for his helpful advice in the preparation of the manuscript.

A grant from the Swift Canadian Company, Limited, Toronto, is gratefully acknowledged.

### References

1. BALSON, E. W. and LAWSON, A. *Biochem. J.* 30 : 1257-1263. 1936.
2. JOSLYN, M. A. *Ind. Eng. Chem.* 33 : 308-314. 1941.
3. KASS, J. P. and PALMER, L. S. *Ind. Eng. Chem.* 32 : 1360-1366. 1940.
4. LEA, C. H. J. *Dairy Research*, 15 : 369-376. 1948.
5. LEA, C. H. and WHITE, J. C. D. *J. Dairy Research*, 15 : 298-340. 1948.
6. LEVY, M. J. *Biol. Chem.* 105 : 157-165. 1934.
7. LEVY, M. and SILBERMAN, D. E. *J. Biol. Chem.* 118 : 723-734. 1937.

\* One other stale powder was investigated. The results of the Van Slyke and formol amino nitrogen and titration curve experiments were very similar to the results obtained with the heated powder. However, this stale powder was not a normal sample, and therefore the results are not reported. The powder had been used for some previous experiment and a number of its constituents (particularly the fat) had been removed or replaced, and other components had been added.

## THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

### XII. THE HIGH COMPRESSION RATIO OTTO CYCLE GAS ENGINE AND THE ADVERSE EFFECT OF HIGH JACKET TEMPERATURES ON THERMAL EFFICIENCY<sup>1</sup>

By R. O. KING,<sup>2</sup> EDWIN J. DURAND,<sup>3</sup> AND J. ALEX. MORRISON<sup>4</sup>

#### Abstract

Town gas was used as the fuel for the C.F.R. engine during a series of engine trials run at a compression ratio of 10 : 1 and at jacket temperatures of 140°, 212°, 302°, and 351° F. The mixture strength at each jacket temperature was varied from the weakest to the richest on which the engine would run steadily. The object of the trials was (1) to determine the effect of jacket temperature on thermal efficiency and (2) to compare the performance of an Otto cycle engine run at 10 : 1 compression ratio with that of a compression ignition (Diesel) oil engine. The results of the trials show that thermal efficiency decreases as the jacket temperature is raised, that is, the decrease more than offsets the gain due to decrease of heat loss during combustion and expansion. It is indicated by the character of the results and by experiments described earlier that the observed loss of efficiency is due to flameless surface combustion of the fuel during compression. The performance of the C.F.R. engine running on town gas at 10 : 1 compression ratio as compared with that of a compression ignition oil engine running at 12 : 1 was superior in respect of maximum power (I.M.E.P.) developed and range of quality control and not greatly inferior in respect of thermal efficiency.

#### Introduction

It was shown by experiments described in Part VI (3) that town gas, containing hydrogen in large concentration, could be used as fuel for an Otto cycle engine at compression ratios as high as 10 : 1, if precautions were taken to prevent the accumulation in the combustion space of finely divided carbon arising from pyrolysis of the lubricating oil. The power measurements made during the experiments were of a preliminary character but sufficed to show that the increase of compression ratio beyond the 5 : 1 commonly used, made possible by avoidance of nuclear ignition, was accompanied by a commensurate increase in power and thermal efficiency.

The C.F.R. knock testing engine, belt-connected to a d-c. generator, was used for the experiments mentioned. Measurements of power output and friction loss were made consequently by indirect methods and accuracy suffered accordingly. The experimental results of this Part were obtained after a swinging field electric dynamometer had been direct connected to

<sup>1</sup> Manuscript received May 17, 1949.

<sup>2</sup> Contribution from Defence Research Board (Canada) in association with the Department of Mechanical Engineering, University of Toronto.

<sup>3</sup> Research Scientist, Defence Research Board and Honorary Lecturer, Department of Mechanical Engineering, University of Toronto. Lately Director of Scientific Research and Development, Royal Canadian Navy.

<sup>4</sup> Lecturer, Department of Mechanical Engineering, University of Toronto.

<sup>5</sup> Supervisor of Appliance Laboratory, Consumers' Gas Co., Toronto.

the engine, and it is considered that an acceptable accuracy of measurement was attained.

The objectives of the experiments were, (1) to determine if flameless surface combustion during compression would more than offset the gain in thermal efficiency due to raising the jacket temperature and (2) to obtain reliable data for an Otto cycle engine running on town gas at a compression ratio of 10 : 1 for a comparison of the performance with that of a compression ignition (Diesel) engine, in respect of power, efficiency, and range of quality control.

Trials were carried out with the jacket coolant at temperatures of 140°, 212°, 302°, and 351° F., mixture strength being varied over the greatest possible range and optimum ignition timing always being used. The temperature of 140° F. can be taken as that of the jacket coolant in motor car engines; 212° F. is the jacket coolant temperature of the A.S.T.M.-C.F.R. method of knock testing; the higher temperatures of 302° and 351° F. represent jacket coolant temperatures of liquid cooled aircraft engines. The cylinders of air cooled engines attain even higher temperatures.

### Experimental Arrangements and Results

The C.F.R. engine, which had been used for some weeks for fuel testing, was dismantled and all carbon and other deposits removed from combustion chamber surfaces. The combustion space was maintained sufficiently free of the accumulations of finely divided carbon, which promote pre-ignition and detonation, by the cleaning routine described in Parts V (2) and VI (3).

The valves were refaced and hand lapped into the seats. The piston rings were in good condition and free in the grooves, all of which were clean. The ignition system was checked and the breaker points set to the standard 0.020 in. gap. The spark plug was cleaned and the gap reduced from 0.025 in. to 0.012 in. as had been found necessary in earlier experiments at the high compression ratio of 10 : 1. The setting of the micrometer used for measuring compression ratio was checked, and maximum compression pressures corresponding to compression ratio settings were found to be in agreement with standard C.F.R. values. The maximum compression pressure at 10 : 1 compression ratio was 290 lb. per sq. in., measured during trials at 900 r.p.m. and with the jacket coolant at 212° F.

#### *Lubrication*

A commercial grade of lubricating oil, S.A.E. 30, free of additives, was used for engine trials at jacket temperatures of 140° and 212° F. A commercial grade of heavy duty oil, Esso S.A.E. 50, recommended for use with Diesel engine was used for trials made with jacket temperatures of 302° and 351° F.

#### *Jacket Temperatures*

The low temperature was obtained by passing tap water through the jacket. The water entered at the lower end of the jacket at 60° F. and flow was

regulated to maintain a nearly constant outlet temperature of 140° F. The standard evaporative method of cooling, using water, was employed to obtain a jacket temperature of 212° F. The higher jacket temperatures of 302° and 351° were obtained by evaporative cooling, using ethylene glycol suitably diluted with water, an extra section being fitted to the reflux condenser.

#### *Power Measurement*

The belt driven main and auxiliary generators of the C.F.R. unit were disconnected from the engine. The main generator was then driven as a motor from the laboratory d-c. supply and it in turn drove the auxiliary generator which supplies current for engine auxiliaries, such as the bouncing pin and the ignition system. The engine was then direct connected to a d-c. swinging field dynamometer with beam type scale. Thus, brake horsepower was measured. Indicated horsepower was obtained by adding to the observed B.H.P. that required to overcome friction and pumping losses when fuel was not added to the air supply and the engine "motored" by the dynamometer. "Motoring" loss was measured after every set of power observations as soon as possible after stopping the fuel supply. A set of observations comprised 6 power measurements made to determine optimum ignition timing for any particular rate of gas supply (mixture strength). Average values of the horsepower absorbed by friction and pumping losses, described hereafter as L.H.P., were as below,—

140° F. jacket, S.A.E. 30 oil—	1.45 L.H.P.
212° F. jacket, S.A.E. 30 oil—	1.31 "
300° F. jacket, S.A.E. 50 oil—	1.24 "
350° F. jacket, S.A.E. 50 oil—	1.17 "

The relatively great loss at 140° F. jacket temperature is due to the entrance of tap water into the lower end of the cylinder jacket at 60° F.

#### *Measurement of Rate of Gas Consumption*

Measurements were made by members of the technical staff of the Consumers' Gas Company of Toronto, using a standard dry meter especially fitted and calibrated for accurate measurement.

#### *Calorific Value of the Town Gas*

The composition and calorific value of Toronto town gas are closely controlled. The composition remained constant during the engine trials at jacket temperatures of 212° F. and higher, made on successive days, but differed slightly from that during the trial at 140° F. jacket temperature made some weeks earlier, as shown by the data of Table I.

The higher calorific value of the gas used for the trial at 140° F. jacket temperature, determined by calorimeter in the Gas Company laboratory, was 465.1 B.t.u. per cu. ft. and the corresponding lower calorific value obtained by calculation was 422.2 B.t.u. per cu. ft. Values obtained similarly for the gas when used later at the higher jacket temperatures were 470 and 427



TABLE I  
COMPOSITION OF TORONTO TOWN GAS AT TIMES OF ENGINE TRIALS;  
PERCENTAGE VOLUMES

Constituents	Trial at 140° F., jacket temperature	Trials at higher jacket temperatures
Hydrogen	48.3	47.4
Carbon monoxide	23.3	21.7
Methane	11.0	12.4
Nitrogen	7.1	7.6
Carbon dioxide	3.7	4.2
Ethylene	3.0	3.8
Ethane	1.8	1.3
Benzene	1.1	0.9
Oxygen	0.8	0.7

B.t.u. per cu. ft. The "lower" values were used for calculating indicated thermal efficiency. All are for the gas at 60° F. and 30 in. of mercury.

#### *Carburetor Arrangement*

The method of admitting gas to the C.F.R. carburetor as used in preliminary experiments is shown by Fig. 1 of Part VI (3). The open end of the gas admission tube was fully exposed to the air oscillations in the induction system of the engine. The oscillations were probably without effect on the accuracy of the gas meter, but as a precaution the open end of the tube was closed and the gas passed through three rings of small holes in the wall of the tube. The air heater of the C.F.R. engine was left in place and provided a mixing chamber for the gas and air.

#### *Ignition Timing for Maximum Power*

The required ignition timing at constant engine speed and compression ratio varies with jacket temperature and mixture strength. Air and gas were both supplied to the engine at atmospheric pressure. The ignition advance required for the maximum power obtainable for a particular rate of gas consumption can be determined only by experiment. Thus the brake horsepower developed when a particular mixture was used was measured at a series of ignition timings giving rising and falling power. The optimum timing was then obtained from a plot of the results.

The method is illustrated by the graphs of Fig. 1, plotted to determine the optimum ignition timing for 14 rates of gas consumption ranging from that required for the weakest to the richest mixtures on which the engine would run steadily. It will be seen by reference to the graphs that optimum ignition timing varies over a wide range, and is somewhat sharply defined at any particular mixture strength. Thus at the weakest mixture on which the engine would run continuously, given by a rate of gas consumption of 47.5 cu. ft. per hr., optimum timing was 44° advance and output was 1.92 B.H.P. The maximum power output of 4.06 B.H.P. was obtained at a rate of gas consumption of 92.5 cu. ft. per hr., and optimum ignition timing was then 13.5° advance. The graphs for mixtures richer than that required for maxi-

mum power are given separately in the right hand top corner of Fig. 1 to save confusion. They show, as usually found, that optimum ignition timing varies less with mixture strength on the rich than on the weak side of the maximum power mixture strength.

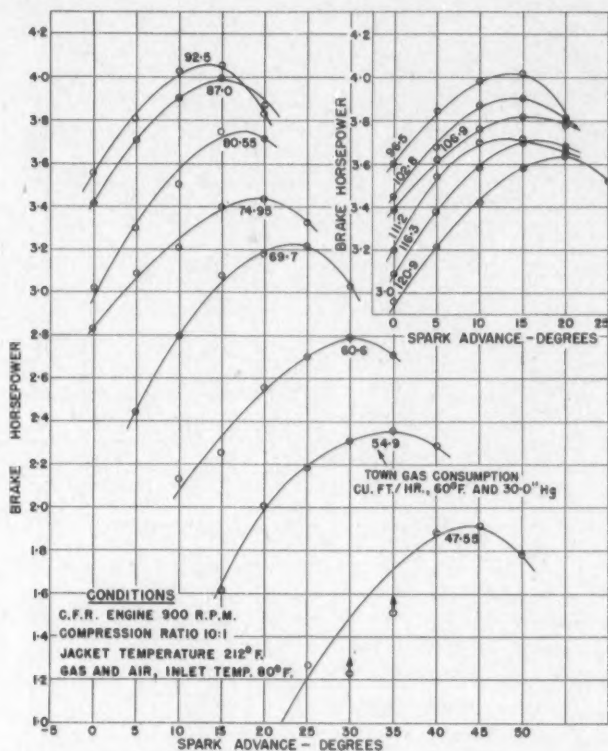


FIG. 1. Graphs for the determination of optimum ignition timing for each of the 14 rates of gas consumption required for the set of trials made at a jacket coolant temperature of 212° F.

The experimental results required for the graphs of Fig. 1 were obtained when the jacket coolant temperature was 212° F. Similar sets of graphs were obtained for jacket coolant temperatures of 302° and 351° F. and for a jacket coolant temperature (outlet) of 140° F.

#### *Brake and Indicated Horsepower, Mechanical Efficiency, 212° F. Jacket Coolant Temperature, Optimum Spark Advance*

The experimental results given by the graphs of Fig. 1 were used to plot the graphs of Fig. 2. Graph A of the figure gives the relation between optimum spark advance and rate of gas consumption and Graph B the corresponding brake horsepower. Graph C, for indicated horsepower, represents the brake horsepower plus the horsepower (L.H.P.) lost in overcoming mechan-

ical and fluid friction, amounting to 1.31 B.H.P. at the jacket coolant temperature of 212° F. Graph D, for mechanical efficiency, gives the percentage relation of brake to indicated horsepower. It will be noted that the value at maximum power output is approximately 76%, a reasonable value in view of the engine's not having been designed for high output and low friction loss.

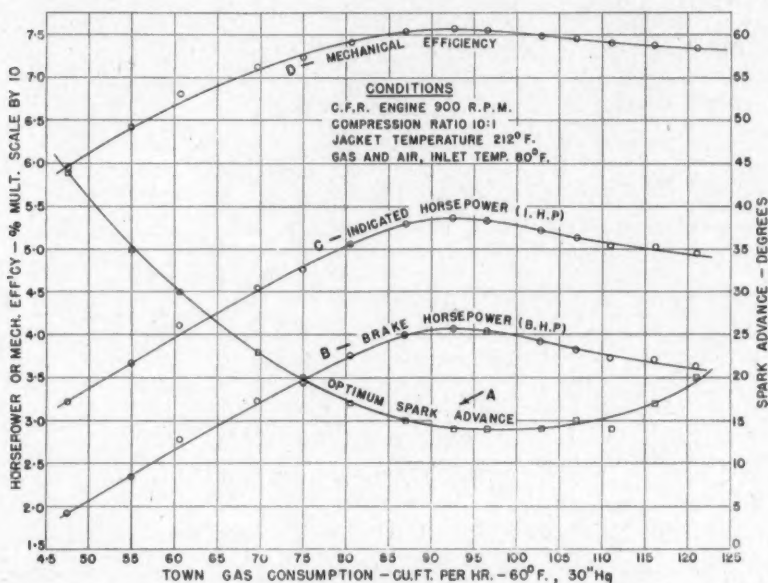


FIG. 2. Mechanical efficiency and brake and indicated horsepower at optimum spark advance—jacket coolant, 212° F.

Indicated or brake mean effective pressures can be obtained by multiplying values given by Graphs C and B by the factor 23.4. Thus I.M.E.P. at maximum power output was 125 lb. per sq. in.

#### Indicated Thermal Efficiency and Power

The internal combustion engine, being noncondensing, is restricted to converting into work some part only of the "lower" heat value of the fuel used. It is necessary therefore to use that value for calculations of thermal efficiency if comparable results for a variety of fuels are to be obtained, because the difference between the lower and higher values varies with the nature of the fuel.

Similarly, when the efficiencies of a variety of engines are compared it is necessary to take into account the total power developed, because the fraction used in overcoming friction varies with design and operating conditions. The total is represented by the indicated horsepower or by the indicated mean effective pressure.

Thus, considering as an example a particular set of engine trials at 900 r.p.m., the jacket coolant at 212° F. and compression ratio 10 : 1, the data used for the calculation of indicated thermal efficiency were as follows,—

Metered rate of gas consumption, 96.6 cu. ft. per hr.

Lower calorific value of the gas at 60° F. (520° R.) and 30 in. of mercury barometric pressure, 422 B.t.u. per cu. ft.

Gas temperature at meter, 73.7° F. (533.7° R.)

Barometric pressure, corrected for temperature, 29.33 in. of mercury

Brake horsepower by dynamometer, 4.06

Friction horsepower (L.H.P.) by dynamometer, 1.31

Indicated horsepower by addition, 5.37

The rate of heat input to the engine is then,—

$$422 \times \frac{520}{533} \times \frac{29.3}{30.0} \times \frac{96.6}{60} = 646 \text{ B.t.u. per min.}$$

and the equivalent ft. lb./ per min. =  $646 \times 778$

The rate at which heat is converted into work is

I.H.P. (5.37)  $\times$  33000, ft. lb. / per min.

and per cent indicated thermal efficiency

$$= 100 \times \frac{5.37 \times 33000}{646 \times 778} = 35.2$$

#### COLLECTED RESULTS OF ENGINE TRIALS

The results of trials made with a jacket coolant temperature of 212° F. are given by the graphs of Fig. 3. They are plotted on a brake horsepower base extending from the minimum power at which the engine would run steadily to the maximum power that the engine would develop. The obtainable range of B.H.P. is shown by the vertical broken lines. It will be noted that power reaches a maximum for a particular rate of gas consumption and then diminishes as the rate is further increased. Thus the familiar consumption "loop" is obtained.

Indicated thermal efficiency attains relatively high values at weak mixtures, decreases slowly until the mixture strength for maximum power is reached, and then very rapidly with further increase in mixture strength. Then as power decreases at the same time, an indicated thermal efficiency "loop", as shown by the relevant graph of the figure, is obtained.

The results of trials made with a jacket temperature of 351° F. are presented similarly by the graphs of Fig. 4. The similar graphs for trials made at 140° and 302° F. are not reproduced because of space limitation.

The features of special interest in respect of the trials made at the four jacket coolant temperatures of the experiments are exhibited by the graphs of Fig. 5. The *A* graphs are consumption loops, and *B* graphs indicated thermal efficiency loops. They show in a striking way the progressive de-

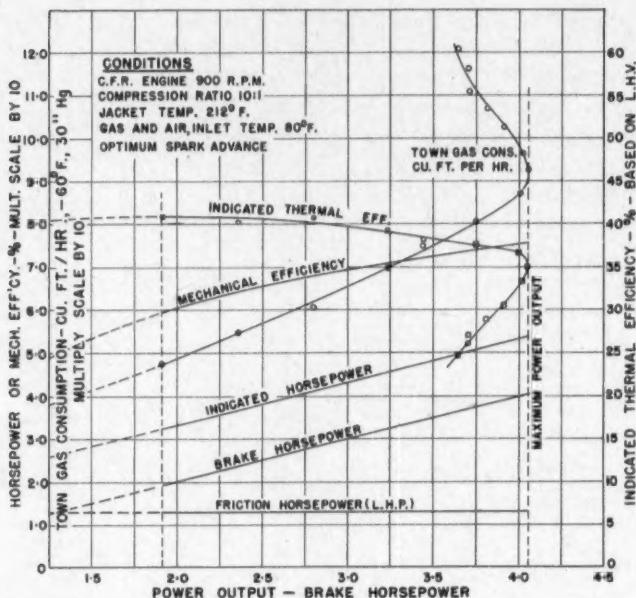


FIG. 3. Graphical presentation of the results of trials made with the jacket coolant at 212° F.

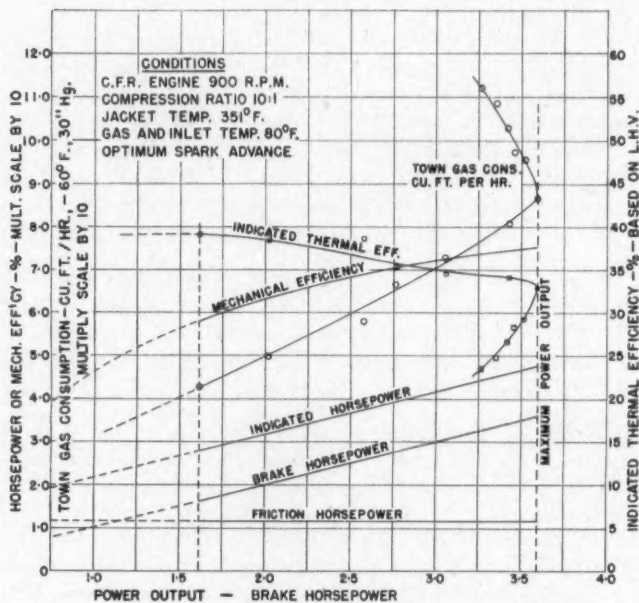


FIG. 4. Graphical presentation of the results of trials made with the jacket coolant at 351° F.



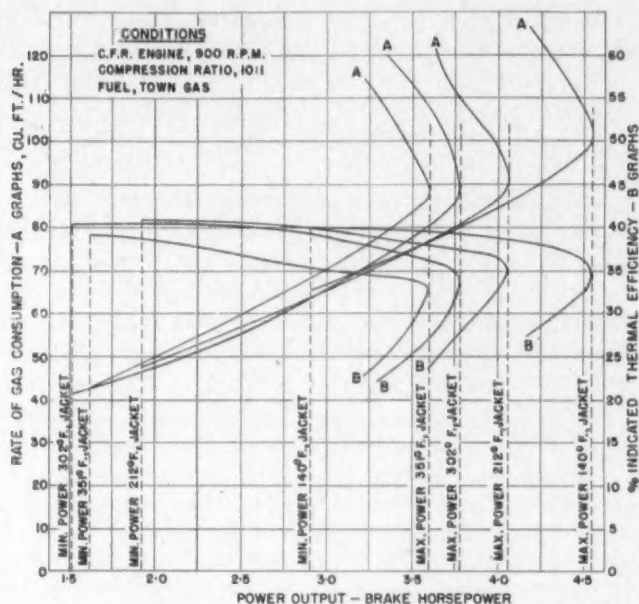


FIG. 5. Consumption loops given by A graphs and indicated thermal efficiency loops by B graphs; for trials made with jacket coolant temperatures of 140°, 212°, 302°, and 351° F.

crease of indicated thermal efficiency and power as jacket coolant temperature is raised from 140° to 351° F. Maximum and minimum powers obtained for each jacket coolant temperature are shown by the vertical broken lines. It will be noted that a relatively high value of minimum power was obtained when the jacket coolant temperature was 140° F. This anomalous result is thought to be due to ignition failure at weaker mixtures.

### Summary and Discussion of Experimental Results

It was not considered possible, prior to the experiments described in Parts V (2) and VI (3), to operate an Otto cycle engine on hydrogen or town gas at a compression ratio of 10 : 1, except when using weak mixtures and consequently obtaining relatively low values of mean effective pressure. Thus, there are not extant any engine trial results for Otto cycle engines with which the experimental results given in this Part can be compared. Recourse must therefore be to the trial results of the compression ignition type of the Diesel engine. The most comprehensive described trials of that type of engine are, so far as known, those by H. B. Taylor (8, pp. 35-85). Data are given for trials run at 12 : 1 compression ratio and speeds of 800 and 1000 r.p.m. and with injection timing fixed or advanced progressively with decrease in mixture

strength. A comparison of the C.F.R. Otto cycle engine trial results with those given by Taylor for the compression ignition engine are therefore of interest although weighted in favor of the latter by the higher compression ratio of 12 : 1 at which they were run. The temperature of the jacket coolant is not mentioned in Taylor's paper but can be assumed to have been that generally used, namely, 60° C. (140° F.).

#### *Thermal Efficiency as Affected by Jacket Temperature*

An increase in jacket temperature, by diminishing heat loss during the combustion and expansion periods, should give rise to a small increase in thermal efficiency. The possibility that the increase might be more than offset by the adverse effect of surface oxidation of the fuel has not heretofore been considered, the established (textbook) view being that "no significant surface reaction occurs in the engine" (1, p. 2934).

The adverse effect of flameless surface combustion on the power developed by an Otto cycle engine running on gasoline was shown by the experiments described in Part XI (4). The experiments of this Part were made to determine if a similar effect would be obtained in suitable conditions if the engine were run on town gas containing a large proportion of hydrogen, which reacts with metallic oxide at relatively low temperatures to form steam. The experimental results obtained accordingly are summarized in Table II. The data given for jacket coolant temperatures of 212° F. are from the graphs of Figs. 2 and 3. The data relating to other jacket coolant temperatures are from similar graphs, which are not reproduced because of space limitations.

TABLE II  
INDICATED THERMAL EFFICIENCY AND INDICATED MEAN EFFECTIVE PRESSURE  
AS AFFECTED BY JACKET COOLANT TEMPERATURE

Jacket coolant temperature, ° F.	Max. power		75% max. power		Min. power	
	I.M.E.P., lb./sq. in.	I.T.E., %	I.M.E.P., lb./sq. in.	I.T.E., %	I.M.E.P., lb./sq. in.	I.T.E., %
140	140.4	35	105	40	(102)	(40)
212	125.0	35	94	40	76	41
302	117.0	33.5	88	40	65	40
351	111.0	32.5	83	37	65	39

With reference to Table II, consider first the effect on thermal efficiency of raising the jacket temperature from 140° to 212° F. The estimates by Ricardo (6, p. 87) and Ricardo and Glyde (7, p. 103), which are not based on experiment, led to the conclusion that an increase of from 0.4% to 1.0% would be obtained. This no doubt is an accurate estimate, taking into account heat loss only. The *experimental* results given in Table II show, however, that no change in thermal efficiency occurred within the jacket coolant temperature range 140° to 212° F., the minimum power measurements at 140° F. being disregarded, for the reason already mentioned. It may be

concluded accordingly that the gain due to the lower heat loss during combustion and expansion was just equal to the loss due to surface oxidation of the fuel during compression.

Consider now the effect on efficiency of raising the jacket coolant temperature from 212° to 351° F. There should, of course, be a gain in thermal efficiency due to lower heat loss to the jacket but instead efficiency decreases by 7% at maximum power and by 7½% at three-quarter power. The total loss attributable to surface oxidation would therefore be the sum of the percentages mentioned plus whatever gain there might have been, taking into account the lower heat loss to the jacket.

The smaller efficiency loss of 4.9%, observed when using the weak mixture required for minimum power, is attributed to the decrease in velocity of the surface reaction with decrease in mixture strength.

#### *Thermal Efficiency, Weak Mixtures*

Thermal efficiency should, according to generally accepted theory, approach the Air Standard value as the concentration of fuel in the mixture with air approaches zero. The experimental results obtained with the C.F.R. engine running at 10 : 1 compression ratio indicate, on the contrary, that thermal efficiency attains a maximum value at a mixture strength richer than the weakest on which the engine continues to run. A similar effect was obtained as a result of earlier experiments with town gas [Part VI (3)]. The observed decreases from the maximum, although small, are of sufficient interest to justify further experiments.

#### *Quality Control*

A feature of the Diesel or compression ignition type of Diesel is that power output at any particular speed can be varied over a wide range by varying the rate of fuel supply, that is, the "quality" of the fuel-air mixture. It became of interest, therefore, to determine the degree of quality control obtained when the C.F.R. engine was run at 10 : 1 compression ratio and with jacket coolant temperature varied over a wide range.

Percentage quality control is taken to be:—

$$\frac{\text{Maximum B.H.P.} - \text{Minimum B.H.P.}}{\text{Maximum B.H.P.}} \times 100$$

Relevant data from the C.F.R. engine experiments are set out in Table III.

TABLE III  
QUALITY CONTROL DATA, C.F.R. ENGINE  
10 : 1 COMPRESSION RATIO

Temperature of jacket coolant, ° F.	Max. B.H.P.	Min. B.H.P.	Friction H.P.	Percent Q control
140	4.55	2.91	1.35	36
212	4.05	1.91	1.31	53
302	3.76	1.52	1.24	60
351	3.60	1.61	1.17	55

The relatively low percentage quality control at 140° F. jacket coolant temperature is believed to be due to ignition failure, as already mentioned.

The obtaining of a wide range of quality control depends on continuing ignition as mixture strength is progressively weakened. The spark ignition system of the C.F.R. engine is not especially adapted for use with very weak mixtures, and although the results are somewhat irregular, as would be expected, it is of interest to compare them with those relating to compression ignition engines as given by Taylor (8).

The percentage quality control obtainable with the compression ignition engine was found by Taylor (8) to diminish with speed and to be little affected by injection timing. Relevant data, taken from page 47 of the reference quoted, are given in Table IV.

TABLE IV  
QUALITY CONTROL DATA, COMPRESSION IGNITION ENGINE,  
12 : 1 COMPRESSION RATIO

Engine r.p.m.	Max. B.H.P.	Injection degrees advance	Min. B.H.P.	Injection advance	Percent <i>Q</i> control
800	64.6	11.5	30		54
800	65.0	12.5	30	31.5	54
1000	80.0	12.0	40		50
1000	79.5	12.0	40	29.5	50

The percentage quality control for the compression ignition engine if run at 900 r.p.m. can be taken as 52. The Otto cycle C.F.R. engine run at that speed and at the lower compression ratio of 10 : 1 affords quality control of 53, 60, and 55% for jacket temperatures of 212°, 302°, and 351° F. respectively.

Quality control is determined by the spread between maximum and minimum brake horsepower (B.M.E.P.). The minimum cannot be greater than the B.H.P. required to overcome friction and pumping losses and may be more nearly reached with the Otto cycle engine by improving spark ignition at weak mixtures. The maximum can be the greater for the Otto cycle engine because of the inability of the compression ignition engine effectively to utilize the mixture strength required for maximum power.

#### *Volumetric Efficiency, Spark Advance*

The engine was always run at constant speed and compression ratio, and any decrease in volumetric efficiency observed on raising the jacket temperature would be due to the consequent heating of the induced charge. The extent of the decrease for a particular increase of jacket temperature would depend mainly on the turbulence and thermal conductivity of the gas-air mixture entering the cylinder. The mixture enters the cylinder of the C.F.R. with a high degree of turbulence because of high velocity attained in passing through a somewhat restricted inlet valve opening, and the gas-air mixture

containing hydrogen in large proportion is of relatively high thermal conductivity. The conditions of the engine trials were therefore such that a large decrease in volumetric efficiency would be expected. Moreover, the increase in charge temperature due to increasing the jacket temperature would give rise to an increase in compression temperature, a corresponding increase in rate of flame propagation after spark ignition, and a consequent decrease in optimum spark advance. Relevant data collected from the experimental results are set out in Table V.

TABLE V  
EFFECT OF JACKET TEMPERATURE ON VOLUMETRIC  
EFFICIENCY AND OPTIMUM SPARK ADVANCE

Jacket coolant temperature, ° F.	Maximum I.H.P.	Gas consumption cu. ft./hr.	Spark advance
140	6.00	102	16°
212	5.40	91.5	14°
302	5.00	88.5	8°
351	4.75	87	4°

When the engine charge is heated during induction, volumetric efficiency diminishes and indicated power decreases in the same proportion if speed and compression ratio remain constant, according to a discussion by Pye (5, p. 240), of experiments by Ricardo. On this basis the decrease of maximum I.H.P. from 6.00 to 4.75, Table V, indicates a large decrease of 20.8% in volumetric efficiency. The method of calculation is based necessarily on the generally accepted view that indicated thermal efficiency does not *diminish* with increase of jacket temperature. It has been shown, however, Table II, that a decrease of 7% was obtained on increasing jacket coolant temperature from 140° to 351° F. Thus of the total decrease of 20.8% in I.H.P., 13.8% represents that due to decrease of volumetric efficiency.

The change in volumetric efficiency can be calculated by another method. Thus, when the engine charge is gas and air, both being supplied at the same temperature and pressure, the rate of consumption of either is proportional to volumetric efficiency *if mixture strength remain constant*. It may safely be assumed that the mixture strength for maximum power is invariable. With reference to Table V, rate of gas consumption at maximum power diminishes from 102 to 87 cu. ft. per hr., that is, by 14.7% when the jacket coolant temperature is raised from 140° to 351° F. The decrease in volumetric efficiency of 14.7% agrees as well as could be expected with the value of 13.8% deduced from observed changes in power and efficiency.

#### *Optimum Ignition Timing*

The decrease in optimum spark advance as jacket temperature is raised is given in Table V and reflects the increase in rate of flame propagation as compression temperature increases with increase in the temperature of the gas-air mixture at the beginning of compression. The result, so far as engine



operation is concerned, is that the usual effects of excessive spark advance, namely, loss of power accompanied by rough running and knock, are obtained for a relatively small advance beyond the optimum value.

### Concluding Comment

#### *The Adverse Effect of Surface Combustion on Thermal Efficiency*

The decrease of thermal efficiency obtained on raising the temperature of the jacket coolant of the C.F.R. engine is attributed to the effect of flameless combustion of hydrogen on oxide coated surfaces, to produce steam during compression. The decrease of efficiency becomes greater as mixture strength increases because the velocity of the surface reaction increases accordingly. Thus the decrease in indicated thermal efficiency, Table II, is 7% at the mixture strength for maximum power. It is 10.3%, that is, 50% greater for the richer mixture obtained on increasing rate of gas consumption by 20%. The adverse effect on thermal efficiency due to surface oxidation is similar to that described in Part XI (4), obtained when surface oxidation of liquid fuel vapor to steam and carbon dioxide occurred on a metal surface maintained in an oxidizing atmosphere by continuous decomposition of a metallic antiknock.

It is to be noted that the conclusion in respect of the cause of the decrease in thermal efficiency with increase in jacket temperature is based on the somewhat indirect evidence afforded by earlier experiments, mainly those described in Part XI (4). Further experiments made in a manner to eliminate surface combustion would therefore be of interest.

#### *Otto Cycle Compared with Compression Ignition (Diesel) Performance*

Combustion in the compression ignition (C.I.) engine leaves unused from 20 to 25% of the air in the cylinder charge. This is approximately the percentage of the air displaced when town gas in "correct" proportion with air is used as the fuel for an Otto cycle engine. Combustion of the fuel, especially when rich mixtures are used, is the more nearly complete in the Otto cycle engine because of the homogeneity of the mixture with air. It would be of interest to compare performances on the basis of the same compression being used. A comparison can however be made at present on the basis of 10 : 1 compression ratio only and 900 r.p.m. for the C.F.R. Otto cycle engine and 12 : 1 compression ratio and 1000 r.p.m. for the C.I. engine. The data for the "best" performance of the C.I. engine used by Taylor (8) are given (page 47 of the reference). The maximum cylinder pressure was 800 lb. per sq. in. and injection timing was advanced as load was reduced.

The maximum I.M.E.P. obtained by Taylor was 133.7 lb. per sq. in., with an indicated thermal efficiency of 38.3%. The corresponding figures for the C.F.R. Otto cycle engine were 140.4 and 35%.

The I.M.E.P. obtained by Taylor at the weakest usable mixture strength was 77.5 lb. per sq. in. with an indicated thermal efficiency of 46.4%. The

corresponding figures for the C.F.R. engine were (at 212° F. jacket temperature) 76 lb. and 41%.

The C.F.R. Otto cycle engine was somewhat superior in respect of the important feature of quality control, as shown by the data of Tables III and IV.

### Acknowledgments

The experimental work was carried out with the co-operation of Prof. E. A. Allcut, Head of the Department of Mechanical Engineering, University of Toronto, and Assistant Professor W. A. Wallace. Special acknowledgment is made of the assistance of Mr. George Southall of the laboratory staff of the Consumers' Gas Company, who carried out the long series of gas supply measurements. Assistance was also given in the course of the experiments by Messrs. C. C. Li, E. H. Dudgeon, W. E. Morley, and H. W. M. Mar, all members of the staff of the Department of Mechanical Engineering.

### References

1. BEATTY, H. A. and EDGAR, G. *In The science of petroleum Vol. 4, Edited by A. E. Dunstan, Oxford University Press, London, New York, Toronto. 1938.*
2. KING, R. O., WALLACE, W. A., and MAHAPATRA, B. *Can. J. Research, F, 26 : 264-274. 1948.*
3. KING, R. O., WALLACE, W. A., and MAHAPATRA, B. *Can. J. Research, F, 26 : 366-373. 1948.*
4. KING, R. O. and DURAND, E. J. *Can. J. Research, F, 27 : 347-358. 1949.*
5. PYE, D. R. *The internal combustion engine. 2nd ed. Oxford University Press, London. 1937.*
6. RICARDO, H. R. *The high speed internal combustion engine. Blackie & Son Ltd., London and Glasgow. 1931.*
7. RICARDO, H. R. and GLYDE, H. S. *The high speed internal combustion engine. Interscience Publishers, Inc. New York. 1941.*
8. TAYLOR, H. B. *Proc. Inst. Automobile Engrs. (London), 22 : 35-85. 1927-28.*

## RELATIONS OF THIAMINE CONTENT IN SASKATCHEWAN WHEAT TO PROTEIN CONTENT, VARIETY, AND SOIL ZONE<sup>1</sup>

BY E. Y. SPENCER<sup>2</sup> AND M. W. GALGAN<sup>3</sup>

### Abstract

The thiamine content (by a short method) and the protein content of 754 samples of the 1946 wheat crop and 458 samples of the 1947 wheat crop were determined. In 1946 four varieties were tested in each of the four soil zones, while in 1947 three varieties were tested on the Brown and Dark Brown soils and four on the Black and Black-Gray Transition soils. A highly significant positive correlation between thiamine and protein content was found for the two crops. No significant differences between thiamine values of the Thatcher 1946 and 1947 crop were found. Similarly, an analysis of variance for thiamine content of Redman in the Black and Black-Gray Transition soil zones and Rescue in the Brown and Dark Brown soil zones, for the two crop years, showed no significant difference. Of the four varieties, Thatcher, Rescue, Pelissier, and Stewart, grown in the Brown and Dark Brown soil zones, Stewart was significantly higher in thiamine content. The greatest range in thiamine content was 2.73  $\mu\text{gm. per gm.}$  for Thatcher in the Black-Gray Transition soil zone (mean 4.01  $\mu\text{gm. per gm.}$ ) to 9.57  $\mu\text{gm. per gm.}$  for Stewart in the Brown soil zone (mean 6.18  $\mu\text{gm. per gm.}$ ). A highly significant difference was found for varieties grown in different zones for both years. The values decreased as the soil changed from brown to dark brown, to black and degraded black, and finally to gray.

### Introduction

A collaborative study by the Universities of Manitoba, Saskatchewan, and Alberta has shown considerable variation in thiamine content in wheat (11). McElroy *et al.* (5) previously found that the thiamine content of wheat in Alberta was influenced by soil type, and there was a positive correlation between protein and thiamine content. Robinson *et al.* (8) found in the 1946 Manitoba wheat crop a varietal effect on thiamine content but the content was not determined by the soil zone in which the samples were grown. No positive correlation was found between thiamine and protein content. O'Donnell and Bayfield (7) and Whiteside and Jackson (12) also found that there were differences in thiamine content of wheat due to varieties. It was felt desirable to continue the study of the varietal and zonal influences on thiamine content in Saskatchewan especially when a large number of samples of wheat from many parts of the province were available.

The use of a shorter method for thiamine determination became a necessity in order to carry out the extensive survey. Previous work (1, 2, 4) indicated the possibility of using a short method, but it was necessary to adapt it for wheat.

<sup>1</sup> Manuscript received June 18, 1949.

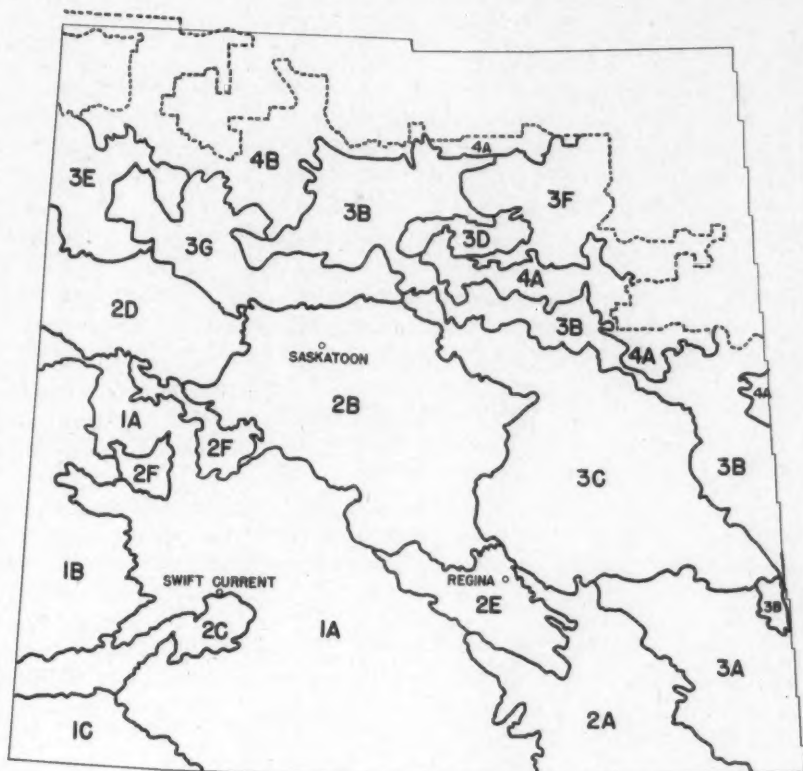
Contribution from the Department of Chemistry, University of Saskatchewan, Saskatoon, Sask., with financial assistance from the National Research Council of Canada and the Saskatchewan Agricultural Research Foundation. Published as paper No. 273 of the Associate Committee on Grain Research of the National Research Council. Presented in part to the Saskatchewan Institute of Agrologists, Saskatoon, May 26, 1949.

<sup>2</sup> Associate Professor.

<sup>3</sup> Graduate Assistant.

### Methods and Materials

The short method as adapted for thiamine determination in wheat was as follows. One gram of wheat ground to pass 1 mm. sieve openings was placed in a 50 ml. volumetric flask, and 25 ml. of sodium acetate buffer, pH 4.6, was added. The sample was digested for one hour in a water bath at 70° C.



Key to Fig. 1—Soil Zones and Subzones.

1. Brown Soils—
  - 1A—Subject to frequent droughts.
  - 1B—Subject to more frequent droughts than 1A.
2. Dark Brown Soils—
  - 2A—Subject to occasional droughts; better moisture conditions than 1A.
  - 2B—Slightly cooler than 2A.
  - 2C—Bench land; cooler, shorter frost-free season and better moisture conditions than 1A.
  - 2D—Higher elevation and distinctly shorter frost-free season than 2B.
  - 2E—Heavy clay soils; more drought resistance than 2A and 2B.
  - 2F—Heavy clay soils; more drought resistance than 1A and adjoining 2B.
3. Black Soils—
  - 3A—Better moisture conditions than 2A.
  - 3B—Shorter frost-free period and better moisture conditions than 3A.
  - 3C—Better moisture conditions than 2B, and cooler than 3A.
  - 3D—Better moisture conditions than 3E.
  - 3E—Shorter frost-free season and better moisture conditions than 2D.
  - 3F—Degraded black and some gray soils; shorter frost-free period than 3D.
- 4A, B. Black-Gray Transition Soils—Short frost-free season.

After it was brought to volume, it was centrifuged for 15 min. at 2000 r.p.m. Aliquots of 5 ml. were placed in reaction vessels, and the procedure was continued as in the regular method used in the collaborative study (11).

A comparison of the results obtained by the above short method and the regular method (11) on 59 samples of wheat was made. The coefficient of correlation ( $r = .81$ ) was highly significant (1% level) and the regression equation was  $E = 1.49 + 0.775x$ , where  $E$  is the estimated value and  $x$  is the value found by the short method.

Using the short method, analyses for thiamine were made on wheat samples grown at various locations in Saskatchewan (3). The 1946 crop consisted of 754 samples of wheat including the varieties Apex, Thatcher, Redman, and Rescue, while the 1947 crop consisted of 458 samples, consisting of the varieties Thatcher, Redman, Rescue, Regent, Pelissier, and Stewart.

The cereal variety zones based on soil type and climatic condition from which wheat samples were obtained are shown in Fig. 1 (9). While this map is basically the soil zone map of Saskatchewan (6), the soil zones have been subdivided because of differences within the zones which effect cereal production but which have not in general resulted in differences in the soil profile.

### Results and Discussion

The thiamine values for wheat ranged from 2.98 to 7.06  $\mu\text{gm. per gm.}$  in 1946 and 2.73 to 9.57  $\mu\text{gm. per gm.}$  in 1947.

The relation between protein and thiamine content was studied by grouping the values according to zones on which the samples were grown. Table I shows a highly significant positive correlation existing between protein and

TABLE I  
RELATION BETWEEN PROTEIN AND THIAMINE IN WHEAT FOR 1946 AND 1947  
CROP IN THE VARIOUS SOIL ZONES OF SASKATCHEWAN

Zone	D.f.	Protein* % (Mean)	Thiamine* $\mu\text{gm./gm.}$ (Mean)	Correl. coeff.	5% Level	1% Level
1946						
1 Brown	205	16.06	4.67	.21	0.137	0.180
2 Dark Brown	192	15.62	4.58	.69	0.139	0.182
3 Black	287	14.93	4.35	.58	0.116	0.160
4 Transition	66	13.70	4.10	.55	0.232	0.302
1947						
1 Brown	48	16.29	4.72	.69	0.274	0.355
2 Dark Brown	77	15.83	4.41	.34	0.220	0.286
3 Black	173	15.10	4.56	.28	0.149	0.196
4 Transition	29	14.65	4.26	.43	0.349	0.449

\*13.5% moisture basis.



thiamine for the 1946 crop in the four zones. Similar results were obtained from the study of protein and thiamine content for the 1947 wheat crop. The relation was further studied by grouping the samples according to varieties. Table II shows a highly significant positive correlation existing between

TABLE II  
RELATION BETWEEN PROTEIN AND THIAMINE IN WHEAT FOR 1947 CROP IN REDMAN,  
THATCHER, RESCUE, AND REGENT

Variety	D.f.	Protein,* % (Mean)	Thiamine,* μgm./gm. (Mean)	Correl. coeff.	5% Level	1% Level
Redman	68	14.80	4.58	.72	0.233	0.303
Thatcher	132	15.57	4.32	.68	0.169	0.220
Rescue	62	15.76	4.56	.65	0.245	0.318
Regent	68	15.36	4.72	.66	0.233	0.303

\*13.5% moisture basis.

protein and thiamine in each of the four varieties of the 1947 crop, Redman, Thatcher, Rescue, and Regent.

In order to study the effect of varieties and soil zones on the thiamine content of wheat, the data were grouped according to variety and zone for each of the years 1946 and 1947 as shown in Tables III and IV.

TABLE III  
THIAMINE CONTENT OF 1946 WHEAT GROUPED ACCORDING  
TO VARIETY AND SOIL ZONE

Zone	Thatcher	Redman	Rescue	Apex	Zonal mean
1	4.60 (52)	4.99 (52)	4.52 (51)	4.56 (51)	4.67 (206)
2	4.57 (48)	4.83 (48)	4.42 (49)	4.52 (48)	4.58 (193)
3	4.29 (72)	4.52 (72)	4.24 (72)	4.34 (72)	4.35 (288)
4	4.05 (17)	4.34 (17)	4.01 (16)	4.00 (17)	4.10 (67)
Varietal mean	4.42 (189)	4.71 (189)	4.34 (188)	4.42 (188)	4.47 (754)

(Mean thiamine values in μgm. per gm., number of samples shown in brackets.)

TABLE IV  
THIAMINE CONTENT OF 1947 WHEAT GROUPED ACCORDING  
TO VARIETY AND SOIL ZONE

Zone	Thatcher	Rescue	Pelissier	Stewart	Zonal mean
1 Brown	4.64 (26)	4.80 (24)	4.98 (24)	6.18 (24)	5.14 (98)
2 Dark Brown	4.33 (38)	4.49 (39)	4.50 (38)	5.45 (38)	4.69 (153)
Varietal mean	4.46 (64)	4.61 (63)	4.69 (62)	5.73 (62)	4.87 (251)
	Thatcher	Redman	Regent		Zonal mean
3 Black	4.32 (58)	4.62 (59)	4.76 (59)		4.57 (176)
4 Transition	4.01 (11)	4.37 (10)	4.49 (10)		4.28 (31)
Varietal mean	4.27 (69)	4.58 (69)	4.72 (69)		4.52 (207)

(Mean thiamine values in μgm. per gm., number of samples shown in brackets.)

It will be noted that the thiamine values were highest for Redman in all zones in 1946. In the 1947 crop, Redman samples were available only in the Black and Transition soil zones and the thiamine values for it were higher than the corresponding values for Thatcher. However, in the same zones, Regent contained the highest thiamine content. In the Brown and Dark Brown soil zones, Stewart contained considerably more thiamine than the other varieties. The thiamine content was greatest in the Brown soil zone. The lowest values were in the Black-Gray Transition soil zone. There was a decrease in thiamine content as the soil changed from brown to gray.

An analysis of variance as presented in Table V shows that the differences between varieties and zones were highly significant. Samples from each of

TABLE V  
ANALYSIS OF VARIANCE FOR THIAMINE IN 1946 AND 1947 WHEAT  
GROUPED ACCORDING TO VARIETY AND SOIL TYPE

Source of variation	1946		1947			
	Zones 1, 2, 3, 4		Zones 1, 2		Zones 3, 4	
	D.f.	Mean sq.	D.f.	Mean sq.	D.f.	Mean sq.
Total	753		250		206	
Varieties	3	4.95**	3	21.19**	2	3.49**
Zones	3	8.09**	1	11.93**	1	2.18**
Varieties x zones	9	0.14	3	0.74	2	0.23
Error	736	0.48	240	1.09	201	0.45

\*\*Significant beyond 1% level.

the four zones were available for Thatcher for 1946 and 1947 (See Tables III and IV). An analysis of variance for Thatcher for each of the two years presented in Table VI shows that there was no significant difference between years, whereas there was a highly significant difference between zones. Similarly an analysis of variance for Redman in the Black and Transition soil, and Rescue in the Brown and Dark Brown soil, for 1946 and 1947, showed no significant difference between years; however, there was no significant difference between zones.

TABLE VI  
ANALYSIS OF VARIANCE FOR THIAMINE IN THATCHER, REDMAN, AND RESCUE  
FOR 1946 AND 1947

Source of variations	Thatcher		Redman		Rescue	
	D.f.	Mean sq.	D.f.	Mean sq.	D.f.	Mean sq.
Total	321		157		162	
Years	1	0.33	1	0.39	1	0.73
Zones	3	2.98**	1	1.03	1	1.02
Error	317	0.41	155	0.46	160	0.57

\*\*Significant beyond 1% level.

A further relation between thiamine content and varietal and regional effects is shown in Table VII, in which the mean thiamine values of the 1947 crop were arranged according to variety and subzones. Where the subzones have been grouped together, this was done because statistical analysis showed no

TABLE VII  
THIAMINE CONTENT OF WHEAT GROUPED ACCORDING TO VARIETY AND  
SUBZONES FOR 1947 CROP

Subzone	Thatcher	Redman	Rescue	Regent	Pelissier	Stewart	Subzonal Mean
1A	4.35 (13)		4.28 (12)		4.42 (12)	5.58 (13)	4.67 (50)
1B	4.92 (13)		5.32 (12)		5.55 (12)	6.90 (11)	5.63 (48)
2A	4.11 (7)		4.32 (7)		4.21 (7)	4.57 (7)	4.30 (48)
2B (S)	4.39 (7)		4.54 (7)		4.50 (7)	5.48 (7)	4.73 (28)
2B (N)	4.63 (9)		4.94 (9)		5.11 (9)	6.39 (9)	5.27 (36)
2C, 2D	4.01 (8)		4.11 (8)		3.63 (7)	4.46 (7)	4.05 (30)
2E	4.45 (4)		4.31 (4)		4.40 (4)	5.31 (4)	4.62 (16)
2F	4.51 (3)		4.64 (4)		5.26 (4)	6.69 (4)	5.33 (15)
3A	4.35 (8)	4.44 (8)		4.59 (8)			4.46 (24)
3B, 3C (E)	4.22 (17)	4.42 (17)		4.57 (17)			4.41 (51)
3B, 3C (W)	4.42 (13)	4.69 (13)		4.84 (13)			4.65 (39)
3E	4.38 (17)	4.92 (16)		5.06 (17)			4.78 (50)
3F	3.90 (3)	4.45 (5)		4.45 (4)			4.31 (12)
4A, 4B	4.01 (11)	4.37 (10)		4.49 (10)			4.28 (31)
Varietal mean	4.36 (133)	4.58 (69)	4.61 (63)	4.72 (69)	4.69 (62)	5.73 (62)	4.52 (258)

(Mean thiamine values in  $\mu\text{gm. per gm.}$ , number of samples shown in brackets.)

differences between them. Similarly, where the subzones have been split (e.g., 2B (N) and (S)) statistical analysis indicated that there was a significant difference in the values for the regions.

Differences between zones might be attributable to either nutritional or climatic effects or both. Zonal differences in soils are present because of broad climatic differences and are reflected in the soil primarily in the amount of organic matter, soil color, and nitrogen content.

TABLE VIII  
ANALYSIS OF VARIANCE FOR THIAMINE—VARIETIES AND SUBZONES—1947 CROP

Source of variation	Zone 1		Zone 2		Zone 3	
	D.f.	Mean sq.	D.f.	Mean sq.	D.f.	Mean sq.
Total	97		152		175	
Varieties	3	12.07**	3	9.86**	2	3.07**
Subzones	1	22.72**	5	6.93**	4	6.19**
Error	93	1.26	144	0.60	169	0.43

\*\*Significant beyond 1% level.

Differences between the subzones within one zone are largely considered by the cerealists to be due to local climatic factors which are not reflected in the soil profile, but which affect cereal production. Certain exceptions do occur where soil profile differences do exist to justify the subzone separation, e.g., in the Brown soil zone the more droughty B subzone is characterized by gray-brown surface colors and lower organic matter content than the rest of the Brown soil zone (10). Similarly, the C and D subzones of the Dark Brown soil zone are dark brown primarily because of the climatic effects of higher elevations. These have been differentiated as cereal subzones because of a shorter frost-free season.

Whether the observed differences in thiamine contents between soil zones and between subzones are due primarily to nutritional factors associated with the soils, or to moisture relations associated with climate, or both, is a question that cannot be answered at this time. The available meteorological data in this region are by no means sufficient to permit any comparisons on the basis of local climates for one or two years.

The thiamine values for different varieties of wheat appear to be influenced by soil and climatic conditions. The more arid brown soils tend to produce wheat of the highest thiamine content, while the gray soils with good moisture conditions tend to produce wheat with the lowest thiamine content.

In addition, there are significant differences between the various subzones within the zones; 1B (Gray Brown) containing significantly more thiamine than 1A (Brown) and 2C and D, the Dark Brown soils of higher elevation and shorter frost-free period containing less than the rest of that zone. Similarly in the Black soil zone, significant differences exist between the regions of the zone. Whether these differences are due to climatic effects of these particular years or not is unknown owing to unavailability of adequate meteorological data. There also appears to be a consistent varietal difference in thiamine content of wheat.

### References

1. ARNOLD, A. *Cereal Chem.* 23 : 521-527. 1946.
2. HOFFER, A., ALCOCK, A. W., and GEDDES, W. F. *Cereal Chem.* 20 : 717-729. 1943.
3. JUNIOR CO-OPERATIVE VARIETY TESTS. Sask. Co-op. Producers Ltd., Regina, Sask. 1946 and 1947.
4. LEWIS, J. R. and GORHAM, P. R. *Can. J. Research, F*, 25 : 133-139. 1947.
5. MCELROY, L. W., KASTELIC, J., and MCCALLA, A. G. *Can. J. Research, F*, 26 : 191-200. 1948.
6. MITCHELL, J., MOSS, H. C., and CLAYTON, J. S. *Soil Survey Rept. No. 12*, Univ. Sask., Saskatoon. 1944.
7. O'DONNELL, W. W. and BAYFIELD, E. G. *Food Research*, 12 : 212-221. 1947.
8. ROBINSON, A. D., LYND, L. E., and MILES, B. J. *Can. J. Research, F*, 27 : 241-248. 1949.
9. SASKATCHEWAN CEREAL VARIETY COMMITTEE. *Saskatchewan Co-operative Agricultural Extension Programme*. 1948.
10. SOILS DEPARTMENT, UNIVERSITY OF SASKATCHEWAN. Private communication.
11. SPENCER, E. Y., ROBINSON, A. D., MCELROY, L. W., and KASTELIC, J. *Can. J. Research, F*, 27 : 194-198. 1949.
12. WHITESIDE, A. G. O. and JACKSON, S. H. *Cereal Chem.* 20 : 542-551. 1943.

